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FLUORINATION OF POLYMERIC MATERIALS FOR HIGH  
ENERGY DENSITY AQUEOUS AND NON-AQUEOUS  
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**THE ELECTROCHEMICAL FLUORINATION OF POLYMERIC  
MATERIALS FOR HIGH ENERGY DENSITY AQUEOUS AND  
NON-AQUEOUS BATTERY AND FUEL CELL SEPARATORS**

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## SUMMARY

Electrochemical fluorination of polymeric materials for high energy density aqueous and non-aqueous battery and fuel cell separators were investigated experimentally during the sponsored period of this research. We have accomplished the following:

1. A microprocessor aided electrochemical fluorination system was constructed and used to obtain highly reproducible results.
2. Electrochemical fluorination of trichloroethylene in anhydrous hydrogen fluoride at 0°C and constant cell potential was investigated.
3. Exploratory investigation of the electrochemical fluorination of polyvinyl alcohol and polyacrylic acid in anhydrous hydrogen fluoride was also studied.

In the electrochemical fluorination of trichloroethylene, the following major two-carbon-chain products were observed:  $\text{CHCl}_2\text{-CCl}_2\text{F}$ ,  $\text{CHCl}_2\text{-CClF}_2$ ,  $\text{CHClF-CCl}_2\text{F}$  and  $\text{CCl}_2\text{F-CClF}_2$ . The first step in the reaction sequence was determined to be fluorine addition to the double bond, followed by replacement of first hydrogen and then chlorine by fluorine. Polymerization reaction yielded higher molecular weight or possible ring-type chlorofluorohydrocarbons.

In the investigation of the electrochemical fluorination of

polyvinyl alcohol and polyacrylic acid, the chemical fluorination of polyacrylic acid was observed. Both solid substrate and membrane form of these materials were used in this study. The aggregate nature of the substrates in anhydrous hydrogen fluoride made the handling and analyzing of the products rather difficult. Further investigation in this research area is needed.

We have submitted two technical reports for publications related to this research at the end of this grant, and expect to hear from the editors sometime in the near future.

We believe that we have accomplished most of the original objectives outlined in the original proposal of this grant. Furthermore, we have established a unique microprocessor aided electrochemical fluorination system capable of obtaining highly reproducible experimental results.

## I. INTRODUCTION

Fluorine-containing organic compounds are known to be valuable to the chemical industry. For instance, many of the lower molecular weight compounds are useful as refrigerants, dielectrics, fire extinguishing materials and as aerosol propellants. Many fluorine-containing compounds are also useful as intermediates for the production of plastics and synthetic elastomers. In recent years, fluorinated materials have been used for ion-selective membranes and high energy, high current density energy storage (battery) system separators. While the needs of producing fluorinated compounds are obvious in the chemical industry, direct fluorination with elementary fluorine is both expensive and hazardous. Unless elaborate and costly measures are taken to moderate the reaction, poor yields are generally obtained (1). Fluorination by milder fluorinating agents such as metal fluorides requires elementary fluorine to regenerate the fluorinating agent, and that is also expensive. Furthermore, the poor selectivity of direct fluorination may give undesirable products as reported by Cuculo and Bigelow (2). In their investigation, fluorination of acetonitrile by fluorine gas produced no compounds retaining the desired nitrile groups. Hence, shortcomings of conventional fluorination procedures have led investigators to pursue more effective approaches in fluorination.

Electrochemical fluorination is considered a viable alternative to direct chemical fluorination. Historically the application of electrolysis in the synthesis of fluorinated organics goes back to Lebeau and Damines (3) and Lyons and Broadwell (4), who obtained  $\text{CF}_4$  using carbon anodes in different metal fluoride melts. However, the more successful electrochemical fluorination process was invented by Simons (5). The process is operated at low temperature, about  $0^\circ\text{C}$ , and atmospheric pressure using liquid anhydrous hydrogen fluoride (AHF) with or without supporting electrolytes such as alkali metal fluorides. Refinements on this method have been reported by Radimer (6), Ashley and Radimer (7), Fox and Ruehlen (8) and Hsu (9). Electrochemical fluorination has some attractive advantages as a process for preparing fluorinated compounds:

1. Because the process is an electrochemical reaction, the experimental parameters, e.g., voltage and current, are controllable with precision. Therefore, precedent would suggest that the product should be, in principle, controllable.

2. The process employs relatively inexpensive raw materials. The direct source of fluorine is AHF, which is an industrial commodity produced on a large scale and is less expensive than the elementary fluorine used in the chemical process. In addition, hydrocarbon feedstocks and electrical power are of low cost relative to the expensive fluorocarbon products.



3. The process requires relatively simple equipment compared to other types of reactor systems. There is no need for high pressure vessels or for separate cell compartments, resulting in lower capital costs.

4. Electrochemical fluorination is a relatively mild reaction when compared with that of elementary fluorine. Carbon-carbon bond scission takes place to a lesser extent and complete fluorination can be accomplished with retention of original functional groups (e.g.,  $\text{-COF}$ ,  $\text{-SO}_2\text{F}$ ); therefore, resulting in compounds that are difficult to prepare by other methods.

5. Highly fluorinated compounds can be produced directly in a single step which involves two simultaneous processes; formation of a fluorinating agent and fluorination of the compounds.

6. Highly fluorinated products are essentially immiscible in AHF, allowing an easy separation from the latter.

In recent years there has been a genuine interest in the investigation of the fundamental kinetics and the practicabilities of the electrochemical fluorination process. Unfortunately, as Dresdner and Young (10) and Drakesmith and Hughes (11) pointed out, electrochemical fluorination is still an art in many respects and is often thwarted by problems of poor reproducibility, poor chemical yields, low current efficiencies, poor selectivity and low operating current densities. The highly exothermic nature of the reaction and the difficulty in properly handling the AHF present further problems. Typical of these problems are those

reported by Kazakov et al. (12) where 500 fluorination experiments are described and "in practically none of the series of experiments was an acceptable reproducibility of results obtained".

Consequently, though many mechanisms or pathways for the process have been postulated and supported by some experimental data, a general and dominating mechanism is yet to be established. Additional experiments have generated still more controversy rather than agreement.

Hence, it is believed that the investigation of electrochemical fluorination under careful control of the reaction parameters, such as applied potential, operation temperature and reaction time in conjunction with advanced analytical techniques for product analysis will result in a better understanding of the electrochemical fluorination process.

The purposes of this study are to examine the fundamental and practical applications of the electrochemical process. For this purpose the investigation of the reaction path of the electrochemical fluorination of trichloroethylene and an exploratory investigation of the electrochemical fluorination of solid polymeric substrates will be described here.

The electrochemical fluorination of trichloroethylene has been investigated independently by Wolfe (13,14), Hsu (9) and Schmidt and Schmidt (15). There is considerable disagreement over the process pathways between these studies and the limited data reported further inhibits any meaningful interpretation of

the kinetics of the process. Hence, it is the objective of this research to obtain reliable experimental results and, based upon the results, to postulate a reaction path which accounts for the formation of the products in the electrochemical fluorination of trichloroethylene.

The electrochemical fluorination of polyvinyl alcohol and polyacrylic acid was studied. These materials have been used in battery cell separators and ion exchange films for removal of metal cations from dilute solutions (16,17). The addition of fluorine to these polymers may impart a desirable chemical and physical stability to the compounds. Perfluorinated membranes have found applications in hydrogen production, fuel cells, energy storage systems, pollution control devices and catalysis. These membranes are currently produced commercially by several chemical processes (18). The in situ electrochemical fluorination of solid polymeric materials may result in a simpler and more economical method of production. Hence, a preliminary investigation of the feasibility of in situ electrochemical fluorination of solid polymeric materials was undertaken.

In the past years, the availability of microprocessors and small computers has added a new dimension to process control and monitoring in many chemical processes. In this work, a microprocessor aided electrochemical reactor system will be used which permits precise control and monitoring of the process and allows connection of real time experiments to a time sharing computer.

It is believed, with the aid of the microprocessor, highly reproducible experimental conditions can be maintained, resulting in more reliable data. The availability of advanced analytical techniques such as GC-MS and E.S.C.A. will also contribute to a more accurate analysis of the reaction products. Consequently, a better understanding about the electrochemical fluorination processes both in terms of basic fundamentals and practical applicability may be obtained.

## 2. THEORETICAL AND GENERAL BACKGROUND

### 2.1 The Mechanism of Electrochemical Fluorination

The mechanism involved in electrochemical fluorination processes is one of considerable complexity and is not well understood. In considering the possible mechanisms it will be useful to summarize the basic characteristics of the electrochemical fluorination process:

1. The reaction takes place at low temperature, i.e., -10 to +25°C.
2. There are no clear indications that any anode material is as good as nickel.
3. No free fluorine is produced although the preferred working voltage is 5 to 6 volts, which is higher than the oxidation potential of  $2F^- \rightarrow F_2 + 2e^-$  ( $V = 2.85v$ ).
4. The process is slow and the maximum usable current density is very low compared to most electrolytic processes.
5. The reaction appears to have an induction period when new anodes are used and that free fluorine is evolved during this period, even at low voltage.

The operation of the system at low temperature results in the relative slowness of the reaction. Regardless of the exact mechanisms of the process, this could account for the relatively small amount of structural degradation that occurs with some substrates during electrochemical fluorination, as compared with other methods of fluorination.

The most practical anode materials have been nickel or nickel alloys such as Monel (66% nickel) (19,20). Under special circumstances, platinum (15,21,22), carbon or graphite (22) have been used. The use of a porous carbon anode in a solution of composition  $KF \cdot 2HF$  at about  $100^\circ C$  has been shown by Fox et al. (1) to give excellent results in partial fluorination reactions. Anodes made of iron, cobalt (plated on copper), stainless steel, silver and lead fail to show any promising ability for fluorination (19). Nickel, nickel alloys, iron, steel, copper (15,19,23) or platinum (15,21) have been used for cathodes, with nickel and iron being most common. Cathodes made of aluminum, zinc, or lead have had a deleterious effect on the reaction (19).

Methods of chemical fluorination include reaction with elementary fluorine and high-valency metal fluorides. Analogies have been drawn (24,25) between these two methods and the electrochemical method, suggesting that either elementary fluorine or high-valency nickel fluorides serve as fluorinating agents in the electrochemical process. Electrochemical fluorination is almost certainly an anodic free-radical type reaction as demonstrated by numerous observations (26):

1. The products of electrochemical fluorination are often the same or similar to those of chemical fluorination, which is known to be free radical in nature.
2. The electrochemical fluorination of pyridene results in the formation of 2-fluoropyridene. A cationic process would have given 3-fluoropyridene.

3. Products resulting from cathodic reduction with hydrogen have not been observed in typical electrochemical fluorinations.

4. Polymeric products are found adhering to the anode. This cannot be explained with an ionic process.

The following mechanisms have been postulated for electrochemical fluorination processes (26,27):

1. Elementary fluorine is generated electrochemically at the anode and reacts with the organic substrate.

2. Simple high-valent nickel fluorides, such as  $\text{NiF}_3$  and  $\text{NiF}_4$  serve as the fluorinating agents.

3. The organic substrate is oxidized to a cationic species, which breaks down to a free radical, followed by fluorine abstraction from hydrogen fluoride or reaction with a fluorine atom.

4. Complex high-valent nickel fluorides such as  $(\text{SH})_2\text{NiF}_6$  and  $(\text{SH})_3\text{NiF}_6$  (where S represents the substrate) could serve as fluorinating agents.

5. The fluorinating agent is a loose complex of  $\text{NiF}_2$  and atomic or molecular fluorine formed at the anode; fluorination would take place between this complex and the substrate, possibly also absorbed on the nickel fluoride layer.

6. Dissociative chemisorption of the organic substrate occurs followed by reaction with solvent and further electron transfer.

The first scheme has been proposed since the products of electrochemical fluorination resemble what might be expected from a very mild fluorination with free fluorine. However, the role of free fluorine in electrochemical fluorination is not clearly understood. The preferred working voltage for fluorination, 5 to 6 volts, is higher than the oxidation potential of free fluorine, yet in many studies no free fluorine is directly observed. This phenomena leads to the argument that a free fluorine mechanism is not possible. However, counter arguments state that the 2.85v required for the liberation of fluorine is not applicable in electrochemical processes, since it is a calculated value only, based upon thermodynamic data obtained from aqueous solutions (28, 29). It could be argued that free fluorine is not typically observed since the amount of fluorine evolved is always less than the amount of reactive substrate present. However, the fact that fluorine is evolved, even at low voltages during a new anode induction period is difficult to reconcile with the free fluorine idea.

Because nickel has been the only good anodic material used in this process, it has been suggested that the formation of nickel difluoride on the anode surface is evidence in favor of a higher nickel fluoride as the fluorinating agent (24,25). Burdon and Tatlow (26) believed that regardless of the reaction mechanism, nickel difluoride can be formed at the anode. They also rationalized that a fluorination mechanism based on simple high-valent



nickel fluorides is unlikely: first, no simple fluoride of nickel above the difluoride has been prepared with certainty; secondly, fluorine would be evolved before  $\text{NiF}_3$  or  $\text{NiF}_4$  could be formed; and finally, electrochemical fluorination products do not resemble those obtained from reaction with high-valency metal fluorides.

The third mechanism fails to account for the observed induction period of new anodes. The "loose" complex of fluorine radicals on  $\text{NiF}_2$  was proposed by Rogers et al. (30) as the fluorinating agent for  $\text{ClF}_3$ . However, chlorine trifluoride is also fluorinated to  $\text{ClF}_5$  at a glassy carbon anode, suggesting that complex nickel fluorides are not essential for this fluorination reaction.

It is possible to explain most of the experimental facts by the complex high-valent nickel fluoride mechanism. These complexes could form at a potential below that required to liberate fluorine. The evolution of free fluorine could take place until the complex is formed. In addition, Stein et al. (31) demonstrated that nickel [III] and [IV] species can be produced at a nickel anode in liquid AHF. The criticism made above that the products of electrochemical fluorinations are different from those of reactions with high-valency fluorides still exists. However, this may not apply to nickel fluorides. These arguments and others suggest that the role of the nickel fluoride complex in

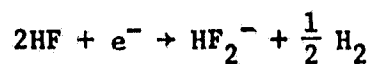
electrochemical fluorination is not clearly understood and that further work in the area is desirable.

## 2.2 The Electrochemical Fluorination of Trichloroethylene

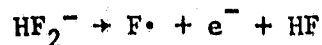
### 2.2.1 Free Radical Versus Ionic Reaction

The electrochemical fluorination of trichloroethylene proceeds by a series of electrochemical and chemical steps. The electrochemical reactions are as follows:

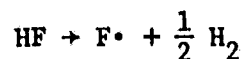
#### Cathodic



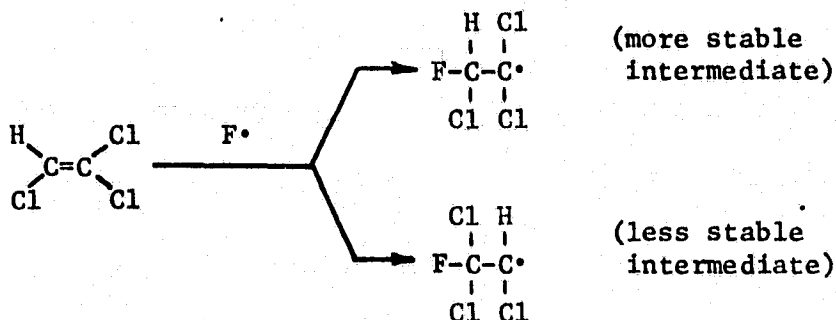
#### Anodic



#### Overall Electrochemical Reaction

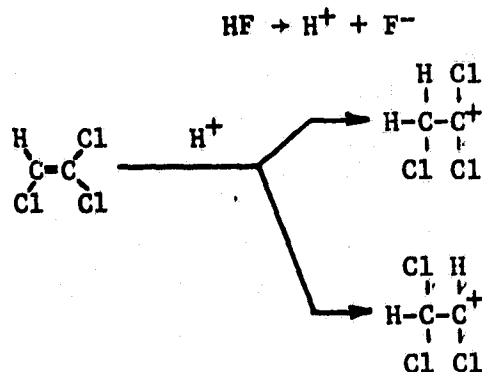


The free radical fluorine then proceeds to react chemically with trichloroethylene to form either of two intermediate free radicals as shown below.



The more highly substituted free radical will be more stable. The intermediates can then extract a fluorine, chlorine or hydrogen from another molecule to form the fluorinated product.

In contrast, an ionic mechanism would proceed through the intermediate carbonium ion:



These intermediates would then proceed to react with an anion to form the reaction products.

### 2.2.2 Selection of Experimental Conditions

In order to obtain meaningful information about the kinetics and mechanisms of electrochemical fluorination processes, careful selection of the experimental parameters is required. The experimental conditions of Hsu's (9) and Wolfe's (13,14) study on the electrochemical fluorination of trichloroethylene, together with those of other electrochemical fluorination processes (5) were examined; and an appropriate selection of the experimental conditions for this work was made. Results from studies under these conditions will provide a basis for comparison and explanation of the pathway and mechanisms of the electrochemical fluorination of trichloroethylene. The rationale for selecting these experimental parameters is described below.

#### 2.2.2.1 Applied Potential

The optimum potential for electrochemical fluorination lies below 10 volts (26); above this value elementary fluorine is most likely to evolve and extensive destruction of the organic substrate and of the anodes takes place (5). Most workers have used voltages between 5 and 7. Dresdner and Young (10) have found that yields from some fluorinations drop rapidly when the potential rises above 5.1V. Hsu applied 6.0V in one case and 7.5-15V in another, while Wolfe used voltages between 5 and 8. It is undesirable to run at too low of a potential since this would prolong the reaction time.

#### 2.2.2.2 Applied Current

Kinetically, the current controls the amount of fluorination that takes place in a given time. Irrespective of the actual fluorinating agent, 1.34 A-hrs/g of fluorine are theoretically required. For any given cell, at a selected applied voltage, the corresponding amperage is determined and no choice of current is possible without varying either the electrode assembly or the concentration of the electrolyte. Hence, for an electrochemical reactor with electrodes of pre-determined area, the potential applied and the substrate concentration are the variables which determine current density. In electrochemical fluorination processes, current density values of 0.0008 to 0.035 A/cm<sup>2</sup> have been reported (5,23,25,32-34). The current

density values in Hsu's study were approximately 0.002 to 0.013 A/cm<sup>2</sup>.

#### 2.2.2.3 Reactor Operating Temperature

There are two opposing factors affecting the choice of temperature. First, the conductivities of solutions in AHF fall rapidly as the temperature drops. This implies that the higher the operating temperature of the reactor, the higher the current that can be passed at the optimum electrode potential. Secondly, AHF boils at 19°C. Claims have been made that electrochemical fluorination can be conducted in the entire temperature range of -80 to +75°C (13,23,35,36). No details have ever been published of fluorination at these extremes. The reactor temperature chosen most frequently is 0°C at atmospheric pressure. Higher temperatures can be used provided that pressure is applied. Wolfe has stated that the electrochemical fluorination of chlorohydrocarbons at low temperature such as -10°C gives a preferential replacement of hydrogen rather than chlorine, whereas at 0°C a more indiscriminate replacement of hydrogen and chlorine takes place. However, no definite conclusion can be drawn about the optimum temperature which almost certainly differs from substrate to substrate. Hsu used a temperature range of 0 to 10°C, while Wolfe reports operation at 0°C.

#### 2.2.2.4 Substrate Concentration

Substrate concentrations between 1 and 50 weight percent have been reported (23,25). When a high substrate concentration is used, anomalous reactions (10) and low yields (37) usually occurred. Although optimum concentrations will differ with different substrates, concentrations greater than 15 weight percent are usually avoided (26). Hsu reported trichloroethylene concentrations of 23 and 47 weight percent, while Wolfe reported a concentration of 47 weight percent.

In a batch process the substrate concentration will decrease as the process progresses. Constant concentrations have been maintained by adding substrate to the reactor at the same rate at which it is fluorinated; however, yield does not seem to be very much affected (38).

#### 2.2.2.5 Conductivity Additives

Hydrocarbons and halohydrocarbons are only slightly soluble (about 3 weight percent) in AHF resulting in non-conducting solutions (39,40). Therefore, conductivity additives are sometimes used to enhance the ionic conductivity of the electrolyte. Their concentration in the electrolyte is usually about 0.5 to 5 weight percent (5,23).

Two types of conductivity additives are commonly used; those that are themselves fluorinated during the process, and those that are not. In the former category are water, alcohol,

pyridine, carboxylic acid and ammonia (5). Alkali-metal and alkaline earth fluorides belong, on the other hand, to the latter type of additives. They are not themselves fluorinated in the reaction, but their use may cause extensive anode corrosion. Both types of additives have another disadvantage that cannot be avoided; they maintain the conductivity of the solution even after the substrate is fully fluorinated.

Hsu and Wolfe reported NaF and KF conductivity additives concentrations of 0.8 to 1.0 weight percent.

#### 2.2.2.6 Electrolyte Mixing

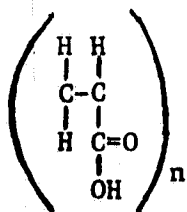
The effect of agitation depends on the substrate to be fluorinated. Agitation did not have much effect on the fluorination of dichloromethane (13). However, it did have a profound effect on the electrochemical fluorination of trichloroethylene (13); without agitation, 50 percent  $\text{CHClF}-\text{CCl}_2\text{F}$ , 30 percent  $\text{CCl}_2\text{F}-\text{CClF}_2$ , and 20 percent other material was formed. Vigorous agitation altered these figures to 82, 12, and 6 percent, respectively.

#### 2.2.2.7 Miscellaneous Parameters

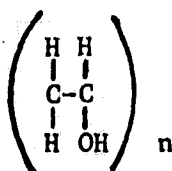
There are other experimental parameters such as pressure, flow rate of carrier gas, etc., that could also be considered in the process. However, it is believed that these parameters are of minor importance in liquid phase electrochemical fluorination reactions.

### 2.3 The Electrochemical Fluorination of Solid Polymeric Materials

Polyacrylic acid (PAA) and polyvinyl alcohol (PVA) are relatively inexpensive, non-toxic, water soluble polymers that can easily be fabricated into transparent films. Their structures are shown below.



PAA



PVA

The PVA films have been utilized as a separator material in alkaline batteries because of their high conductivity in alkaline electrolytes. Although PVA is soluble in water, it is not readily dissolved in such a concentrated alkaline solution. Radiation crosslinking of PVA and PAA has been used to produce water insoluble polymers with improved mechanical properties (16,17). By comparison, PAA films are more conductive than PVA films; however, due to their high concentration of hydrophylic carboxylic acid groups they tend to swell and become weak in alkaline solutions. These carboxylic acid groups, however, provide the PAA films with a high ion exchange capacity. Crosslinked PAA films have also been shown to be effective in removing metal cations from dilute solutions (16). Possibly, radiation crosslinking of a PAA-PVA polymer mixture can lead to an optimum blend of conductivity and physical strength.



The addition of fluorine to the crosslinked PAA and PVA can import additional chemical and physical stability to the polymers. It is expected (41) that the OH group of both polymers will be replaced by fluorine in a chemical reaction with AHF. Hopefully, the electrochemical reaction with AHF will result in replacement of hydrogen by fluorine.

Replacement of all hydroxyl groups and hydrogens in crosslinked PVA would result in a crosslinked polytetrafluoroethylene (PTFE). Although this polymer is nonconductive, its extreme chemical and physical stability results in its many applications. Current processes used for the production of PTFE (e.g., suspension and emulsion polymerization) are quite costly. Hence, the electrochemical fluorination of crosslinked PVA may result in a more economical method of production of a higher strength, possibly clear, PTFE.

The PAA will still be highly conductive if the carbonyl group is retained during the electrochemical fluorination process and thus may find application in battery separators. The conductivity of this polymer may be higher than that of standard membrane materials as a result of its high concentration of functional groups.

### 3. EXPERIMENTAL

#### 3.1 Description of the Reactor System

The reactor system can be separated into two parts: one is the electrochemical reactor and its accessories, and the other is the microprocessor for the control and monitoring of the process.

The electrochemical reactor is a typical Simons' cell (5,9) having a capacity of 500 ml containing a pack of alternate anodes and cathodes fastened together, but insulated from each other. Figure 1 shows the physical structure of the reactor. Nickel electrodes are used in this study and the total surface areas for the cathodes and anodes are each 260 cm<sup>2</sup>. The electrode spacing is 1.6 mm.

A schematic diagram of the complete electrochemical fluorination system is shown in Figure 2. In addition to the reactor, a reflux condenser is incorporated into the system. The condenser can be cooled to -50°C to prevent any serious loss of anhydrous hydrogen fluoride (AHF). An outside jacket on the reactor permits the cooling medium to maintain the reactor at a predetermined operating temperature, i.e., -10 to 10°C. The refrigeration unit (Neslab Endocal) can take ethanol coolant down to -80°C and is used to cool both the condenser and the reactor. In this system, constant temperature operation of the reactor is achieved by means of a temperature controller connected

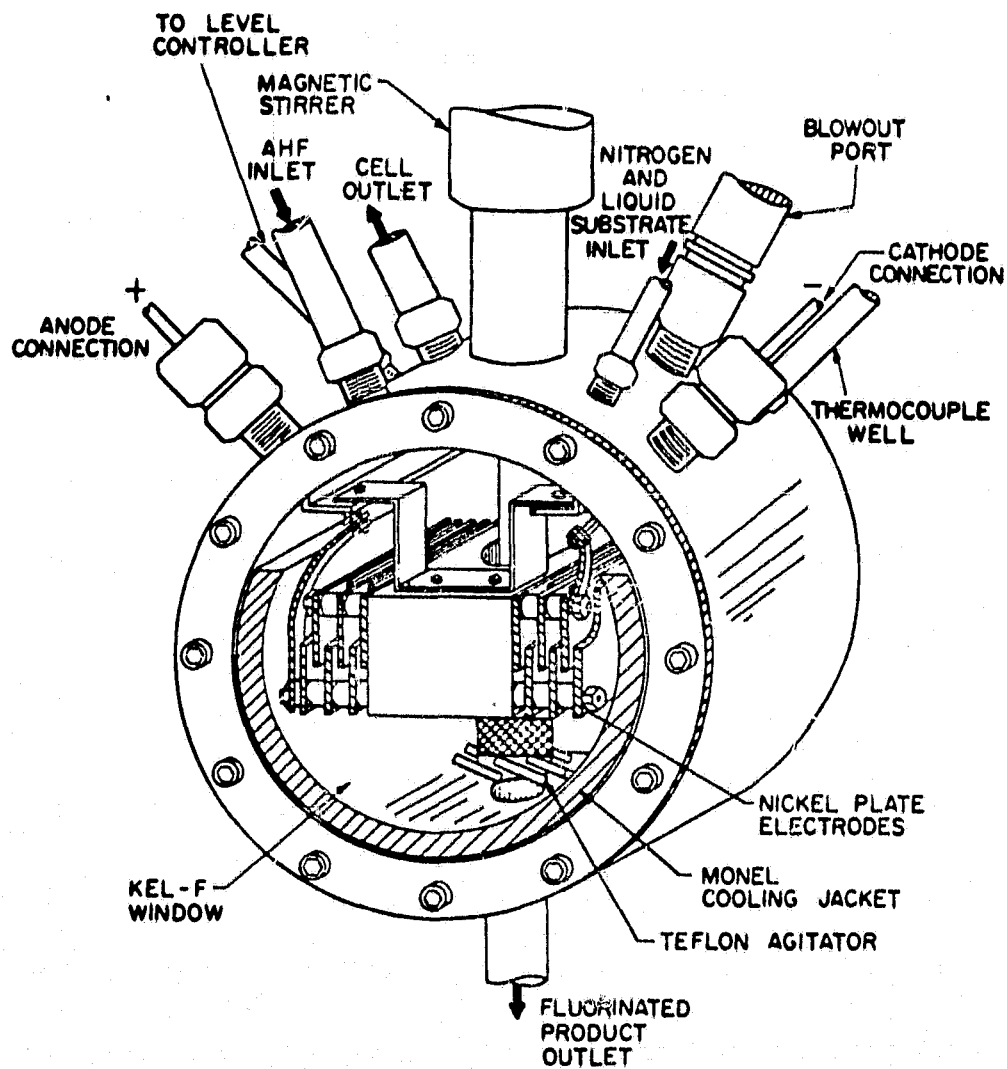


Fig. 1 Physical Structure of the  
Electrochemical Fluorination Reactor

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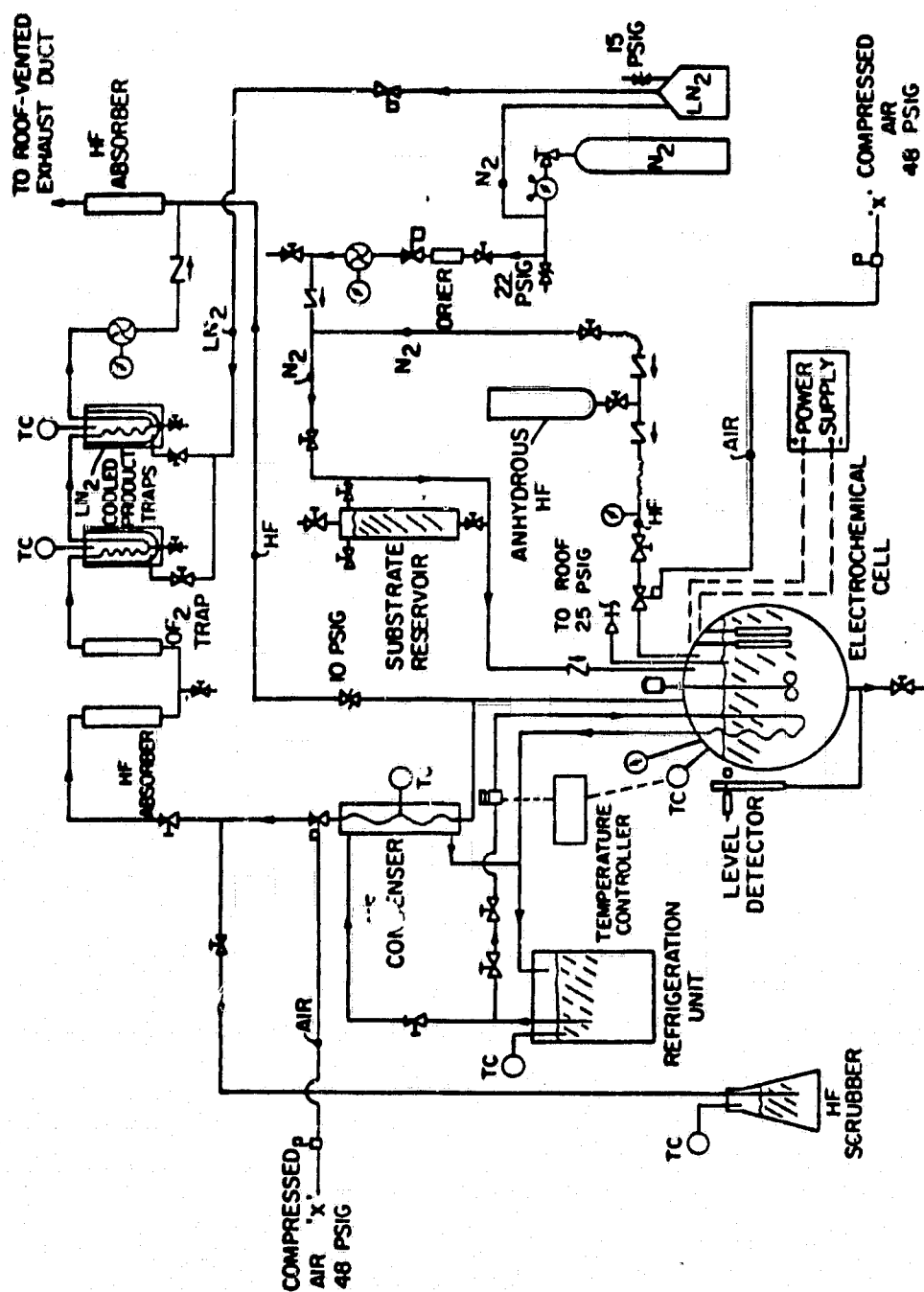


Fig. 2 Schematic of the Complete Electrochemical Fluorination System

to a solenoid valve in the refrigeration line leading to the reactor. Two liquid nitrogen cold traps are included in the exhaust line to remove any condensable products. Electrochemically, the fluorination process can be operated at either a constant voltage or a constant current mode of operation over any preset period of time. A power supply (LAMBDA LES-EE-02-OV) capable of providing voltages of 0 to 18V and currents of 0 to 29 amperes is used for this study. The system can be operated with controlled electrode potential using a high current potentiostat.

Because of the corrosive nature of AHF, the reactor is constructed of Monel. All of the valves and other system components that come into direct contact with AHF are also made of Monel or Teflon. In order to permit direct visual observation or recording of the process, the front window of the electrochemical reactor and the substrate reservoir are fabricated of Kel-F.

Pure nitrogen is used as a carrier gas for the AHF and substrates. Both the AHF and the substrate can be added when the reaction is in progress and when the reactor is under pressure. A scrubber containing a caustic solution is used to neutralize the AHF at the end of a run. The refrigeration unit is also used to heat the cell and evaporate the AHF into the scrubber.

The safety aspect of the operation of this fluorination process is of considerable importance. Thus, absorbers for any

excess AHF and oxygen difluoride are employed after the reflux condenser to assure safety. NaF pellets are used for AHF absorption. Rubber pellets are used in the OF<sub>2</sub> absorber. A maximum pressure of the system is insured by a pressure relief valve ( $6.9 \times 10^4$  pascals) and a relief outlet with a Teflon rupture membrane ( $13.8 \times 10^4$  pascals).

The electrochemical fluorination system is mounted on a metal frame within a Plexiglas shield. The complete unit is located in a test cell within a laboratory designed for hazardous and high pressure work. The test cell is equipped with steel reinforced concrete walls (30.5 cm in thickness) and a large steel stack extending (106.7 cm diameter) above the cell room. Figure 3 shows a photograph of the unit.

The other aspect of this system involves the use of a micro-computer system that: 1) controls and monitors the electrochemical reactor, and 2) allows connection of real time experiments to a time-sharing computer. The basic design criteria and objectives of this system have been described elsewhere (42,43). Basically, the system utilizes a Motorola 6800 (8-bit) microprocessor, chosen because of the ease and flexibility of programming. Figure 4 shows the architectural structure of the microprocessor system.

For monitoring, the system uses an 8-channel analog-to-digital converter. Currently two channels are occupied with two thermocouple scanners, each of which has ten channels. The

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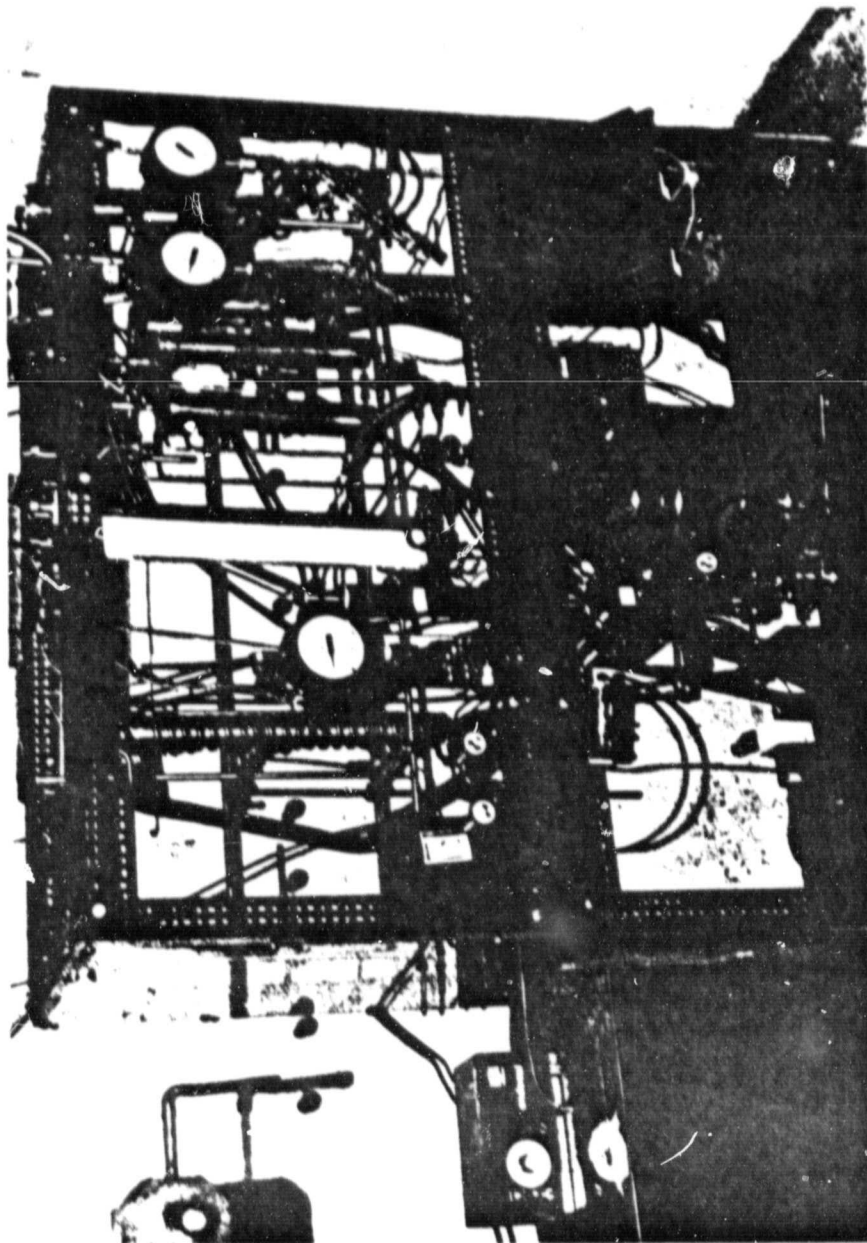
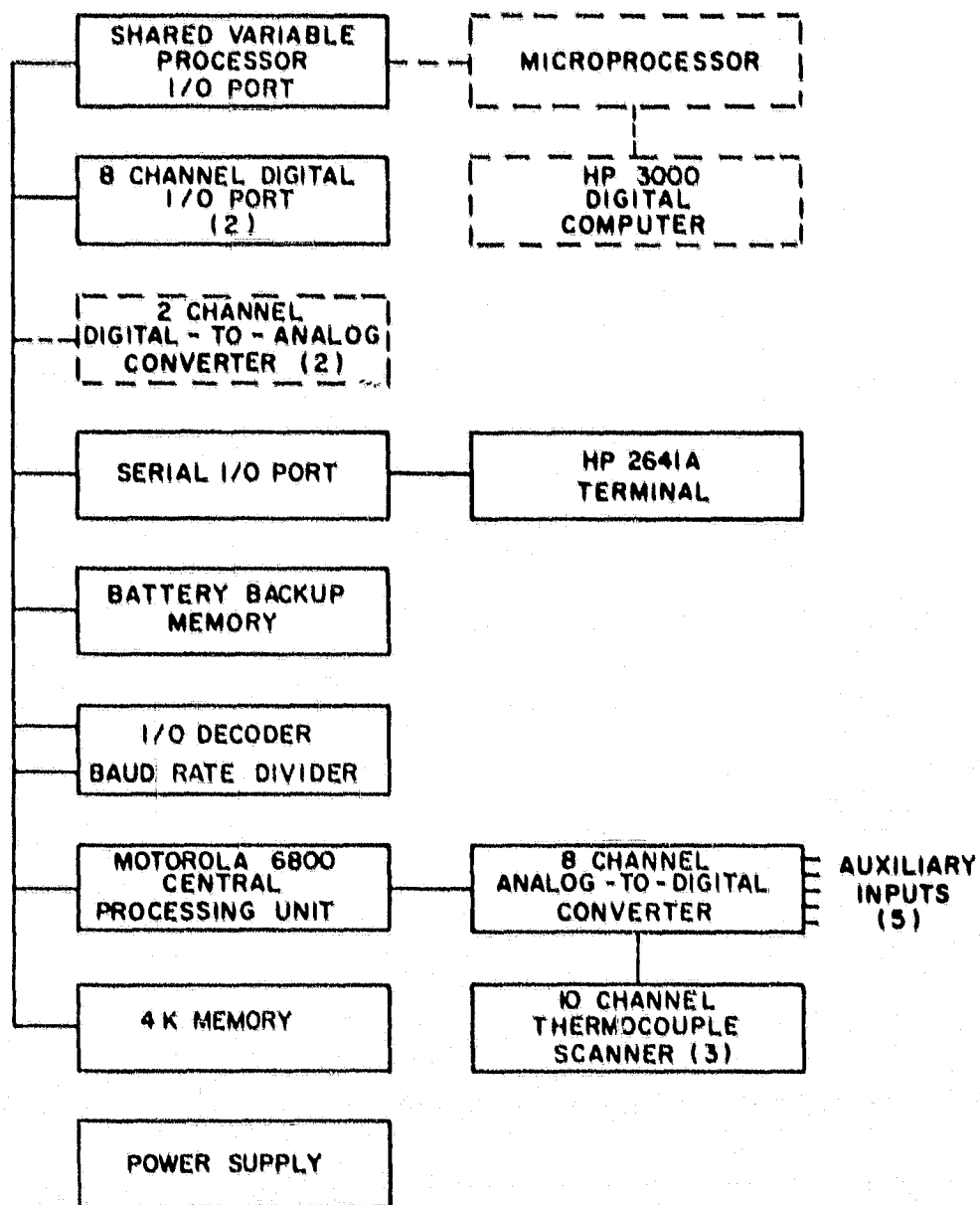


Fig. 3 Photograph of the Electrochemical  
Fluorination System



----- FUTURE ADDITIONS

Fig. 4 Architectural Diagram of the Microprocessor System



thermocouple scanners can be programmed to accept either a thermocouple input or a voltage/current input. The system can handle up to three scanners, giving it the capability of accepting up to 35 thermocouple or millivolt inputs. Besides the measurement of thermocouples, other instrumentation inputs, such as pressure transducers, can be interfaced with the system. A thermocouple linearization table is included in the software, providing good temperature reading and control for low temperature operation. An auto-zero circuit is also incorporated into the thermocouple monitoring system for periodic compensation of zero drifting.

For control, the system also features two 8-channel digital input/output ports. They can be used to register an open or closed position for a solenoid valve or an on or off position for instrumentation such as the refrigeration unit. The microprocessor unit also has the capability of accepting two 2-channel digital-to-analog converters. The baud rate on the serial port can be set to any rate between 110 and 9600 baud. The shared variable processor input/output port is not currently in use but gives the system the capability of interfacing with another microprocessor and a small computer such as the HP-3000 which is available in our laboratory. The HP-3000 can be used for data storage and manipulation.

The microprocessor unit is interfaced with a HP-2641A terminal for control and display of parameters. The user can

select sensors, e.g. thermocouples and pressure transducers, and operational parameters, e.g. voltage, current, and valve positions for monitoring, and display up to 48 parameters simultaneously. The microprocessor can be programmed to scan the data in time intervals of 1 to 99 seconds. It has a 4K memory that stores the thermocouple linearization table and the list of parameters to be displayed. A non-volatile back-up memory is installed that can protect the data for up to 48 hours in the case of a power outage.

The refrigeration unit, power supply, stirrer, pneumatic solenoid valves and valves for the carrier gas and liquid nitrogen can be operated from the terminal. These units can also be operated in the manual mode, providing greater flexibility in operation and control. The terminal is located outside of the test cell, allowing safe operation of the fluorination system.

The reactor can also be operated in a semi-batch mode. A capacitance-type level detector on the cell allows for automatic AHF addition when the level becomes too low. An additional solenoid valve will enable automatic substrate addition. Electrochemical fluorination reactions under potential control are characterized by a drop in current as the substrate is being consumed. A pre-defined current level also can be used as a means for controlling the substrate addition to the reactor. A level sensor in the cold traps allows for automatic liquid nitrogen addition. The microprocessor can be programmed to allow for voltage and current ramping.

### 3.2 Materials

The reactants used in the electrochemical fluorination of trichloroethylene were commercial grade anhydrous hydrogen fluoride (Ideal Gas Products; Union Carbide Corporation; >99.9% pure) and Certified ACS Grade trichloroethylene (Fisher Scientific Co.).

The solid polymeric substrates, polyacrylic acid and polyvinyl alcohol were supplied in powder form by the NASA Lewis Research Center. An inert electronic liquid (3M "Fluorinert" FC-77) was used as a dispersion agent for the solids.

High purity nitrogen (Liquid Carbonic Co., 99.998% pure) was used as a flush gas for both of the above tests. The only other materials in contact with the electrolyte were Teflon, Kel-F, Monel and nickel.

### 3.3 Analysis of Products

Several methods of analysis were used to determine the reaction products in the fluorination of trichloroethylene. A quantitative analysis of the fluorinated products was performed using a Hewlett Packard 5840A gas chromatograph. The column was 254 cm of 0.32 cm diameter stainless steel packed with 20% SP-2100, 0.1% Carbowax 1500 on 100/120 mesh Supelcoport. The oven temperature was 125°C and a helium flow rate of 20 ml/min was employed.

A GC-MS analysis was accomplished by a coupled Varian-MAT-CH-7 mass spectrometer and a Varian 1740 gas chromatograph.

Plots were generated on a Varian SS-200 Data System. The same column described above was used in addition to a 3% SP-2100 column. The oven temperature was held at 25°C for 5 min and then increased to 135°C at a rate of 10°/min. The helium gas flow rate was 30 ml/min. A Varian XL-100 n.m.r. spectrometer was used for the  $^{19}\text{F}$  n.m.r. analysis. Proton n.m.r. was accomplished with a Varian XL-200 n.m.r. spectrometer.

A semi-quantitative elemental analysis of the solid polymer products was accomplished with E.S.C.A. A Varian IEE spectrometer was used. Fluorine and carbon scans were performed.

### 3.4 Procedure

#### 3.4.1 General Procedure

All electrochemical fluorination experimental runs were operated in the batch mode and conducted at a constant voltage. The overall cell potential was held constant throughout the experiments, and no reference electrode was employed. For simplicity, the electrochemical fluorination system was run in the manual mode and the microprocessor system was utilized mainly for the monitoring of parameters in this study. Cell potential, current, reactor temperature, condenser temperature and scrubber temperature were displayed simultaneously on the HP-2641A terminal. Cell current as a function of time was monitored on a strip chart recorder (Houston Instrument, OmniScribe). Current consumption was determined by integrating the area under the chart recorder output by the standard cut and weigh technique.

#### 3.4.2 The Electrochemical Fluorination of Trichloroethylene

The selection of experimental conditions was made in order to provide a means for comparison to the work of Hsu and Wolfe.

In a typical run, the experiment proceeded as follows: Prior to cooling the reactor to the selected operating temperature, 0°C, nitrogen gas was passed through the reactor in order to prevent any water condensation. Otherwise, water could be electrolyzed in the presence of AHF to form oxygen difluoride, a powerful oxidizing agent that might result in explosions when decomposed in bulk or in combination with hydrogen. Oxygen difluoride might also explode when rewarmed after being condensed. Commercial AHF contains a small amount of water as impurity; hence, the electrolysis should be carried out with a nitrogen flush stream to prevent the possible build up of oxygen difluoride in dead space within the reactor. Prior to the addition of AHF, the condenser was cooled to -40 to -50°C, and the reactor to 0°C. A temperature controller maintained the reactor temperature within  $\pm 1^\circ\text{C}$ .

The AHF was added to the reactor and allowed to cool to operating temperature, after which the trichloroethylene was added from the substrate reservoir. The AHF was used either directly as received or electrochemically dried of its water content prior to introducing the substrate. The amount of reactants was chosen so as to give a 6:1 molar ratio of AHF to

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trichloroethylene and to sufficiently cover the electrodes. This corresponds to a substrate concentration of 52 weight percent. A high concentration was used to minimize the percentage loss of reactant resulting from sampling at intermediate times. The two reactants are insoluble; therefore, a level of agitation was chosen to provide a uniform emulsion. Conductivity additives were not used in order to avoid any possible effects on the reaction, regardless if the effects were positive or negative.

A summary of reactions conditions common to all runs is given in Table 1.

TABLE 1  
COMMON REACTION CONDITIONS FOR THE ELECTROCHEMICAL  
FLUORINATION OF TRICHLOROETHYLENE

Reactor Charge	
Trichloroethylene	281 g, 192 ml
Hydrogen Fluoride	258 g, 258 ml
Reactor Temperature	0 $\pm$ 1°C
Cell Voltage	6.00 $\pm$ .05V
Agitation Speed	1000 rpm
N <sub>2</sub> Gas Flow Rate	50 ml/min

Once the reactor contents had reached operating temperature, the experiment was started. The liquid nitrogen cold traps were not required in the experiments and no attempt was made to

collect any gaseous products. When collecting reaction products at intermediate times, the stirrer was turned off temporarily, permitting the denser trichloroethylene phase to settle. Samples were withdrawn through the valve at the reactor bottom. Caution must be exercised to avoid any spillage of the reactant. Small sample sizes ranging from 3 to 8 ml were taken to assure that any variation of the experimental conditions would be minimized. The reaction products were insoluble in water and were neutralized by passing them through a separator funnel filled with 25 ml of a 2N sodium hydroxide solution.

It has been shown that the condition of the anode surface would be critical to the reproducibility of the results (11). Therefore, prior to each run the electrodes were cleaned thoroughly with a liquid sandblaster.

At the end of the run the reactor contents and the reflux condenser were gradually warmed with the refrigeration unit. Additional heat was supplied to the reactor with a hot air blower. The AHF (boiling point:  $19.6^{\circ}\text{C}$ ) was evaporated out of the reactor and bubbled through a sodium hydroxide scrubber. The scrubber consisted of a 10 l vessel containing a 4N NaOH solution, placed within a larger 30 l tank filled with water. The neutralization reaction is highly exothermic and the larger tank was required to conduct heat away from the scrubber. After the AHF was evaporated the remaining fluorinated products were withdrawn.

#### 3.4.3 The Electrochemical Fluorination of Solid Polymeric Materials

In this phase of study three different methods were used to add the solid substrates into the reactor. In the first method, AHF was first added to the reactor and cooled to operating temperature. The substrate was then added through the blowout port on the top of the reactor. The solids aggregated upon contact with the AHF. All the solid substrates studied appeared to be non-soluble or only slightly soluble in AHF. Consequently, the aggregated compound remained on the top of the electrodes or on the impeller blades. A second method of adding the solid substrate consisted of removing the front reactor plate prior to the run and placing the substrate on the reactor bottom. The AHF was then added to the reactor. This caused the solid to aggregate and remain on the reactor bottom. It was believed that the above two methods would not lead to an efficient fluorination process due to the lack of dispersion of the substrates.

A third method yielded the best results. "Fluorinert", an inert perfluorinated organic liquid was used to aid in the dispersion of the solids. This liquid was chosen to prevent the occurrence of any other fluorination reactions. "Fluorinert" was first added to the reactor. The solid substrates were then added through the blowout port. The solids were not soluble in the "Fluorinert"; however, a uniform dispersion was produced by agitation. After the "Fluorinert" was cooled to operating temperature,



the AHF was added while agitating the reactor contents. The substrate aggregated to a lesser degree and formed smaller particles than by the previous methods. Some of it adhered to the electrodes and impeller blades; however, the remainder was dispersed in the reactor. The "Fluorinert" was denser than and insoluble in AHF; therefore, agitation was needed to produce an emulsion.

An attempt was also made to fluorinate the polyacrylic acid (PAA) by first coating it directly on the anode. In this study, a modified form of the electrodes was used and is shown in Figure 5. The electrodes were fabricated from 1.6 mm nickel plate and are spaced 2 mm apart by Teflon washers. Both electrodes have a surface area of  $28.7 \text{ cm}^2$ .

The polymer, in latex form, was applied on both sides of the anode. Tests were conducted with this anode and one in which a PAA film was pressed onto the PAA coating. The PAA film, approximately 0.4 mm thick, was fabricated by spreading the polymer with a Gardner knife. Crosslinking was accomplished after anode coating by exposing the films to ionizing radiation from a linear electron accelerator (Radiation Dynamics, Inc.). The films must contain some water, since hydrogen atoms in the irradiated water are instrumental in the crosslinking reaction (44). A low radiation level of  $1 \mu\text{A}/\text{cm}^2$  was used to avoid burning the film.

The AHF was not electrochemically dried for any of the solid polymer tests. Nitrogen was used as a flush gas, as described

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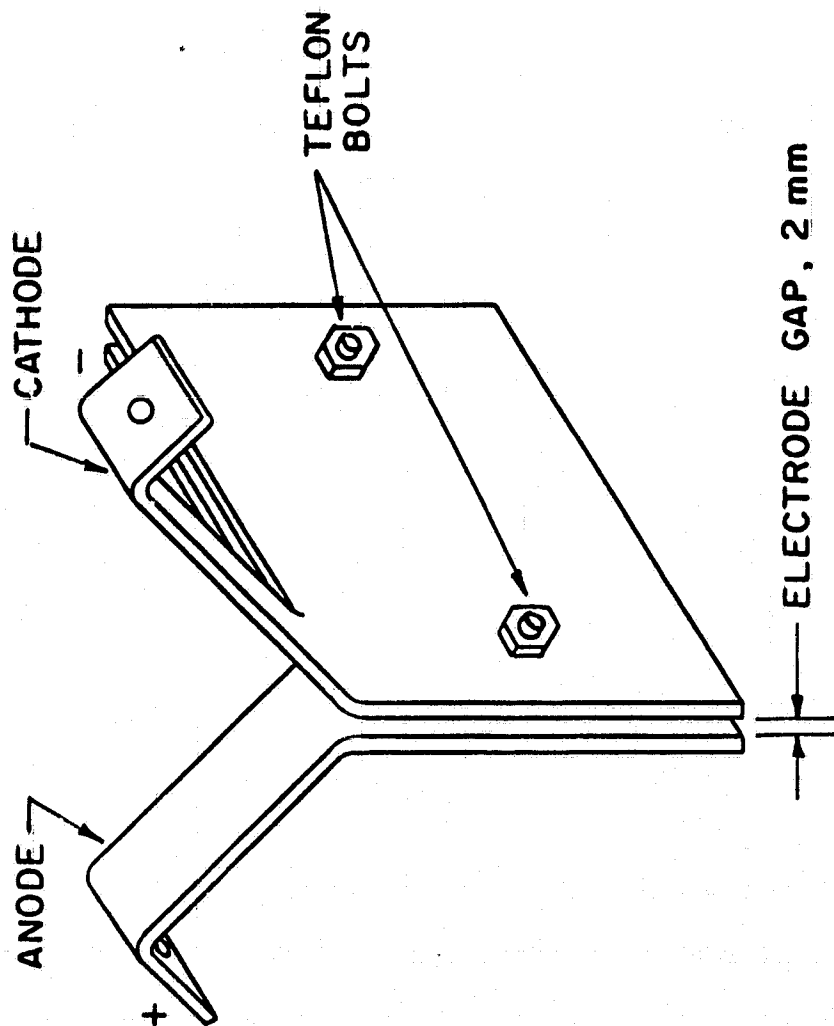


Fig. 5 Electrodes Used in Solid Polymer  
Coating Tests

earlier in the trichloroethylene studies. A summary of operating conditions common to all solid polymer runs is given in Table 2. The agitator was not used with the modified electrodes shown in Figure 5.

At the end of the run, the AHF was evaporated from the reactor and then the "Fluorinert" drained. The front reactor plate was removed, and the solid product was removed from the bottom of the cell or from the surfaces of the electrodes or impeller blades.

TABLE 2

COMMON REACTION CONDITIONS FOR THE  
ELECTROCHEMICAL FLUORINATION OF  
SOLID POLYMERIC MATERIALS

Reactor Temperature	$0 \pm 1^{\circ}\text{C}$
Cell Voltage	$6.00 \pm .05\text{V}$
Agitation Speed	1000 rpm
N <sub>2</sub> Gas Flow Rate	50 ml/min

## 4. RESULTS AND DISCUSSION

### 4.1 The Electrochemical Fluorination of Trichloroethylene

Four runs were conducted under almost identical conditions, in order to assess the reproducibility of the experimental data. The AHF (>99.9% pure) was used as received in these runs. In addition, a comparison run was performed in which the AHF was electrolyzed to remove any residual water for a period of 19 hours before the trichloroethylene was added; this corresponds to a total of 32.1 ampere-hours. Table 3 summarizes the operational conditions and product distributions of the experimental runs. Only the major two-carbon-chain products are considered in this table.

The Freon system for numerical designation of fluorocarbons is used here (45). In this nomenclature system, the last digit is the number of fluorine atoms in the compound, the second last digit is one more than the number of hydrogen atoms, and the third last digit is one less than the number of carbon atoms. For cyclic derivatives, the letter C is used before the identifying refrigerant number. In the case of isomers, differentiating one from another is done by the addition of a letter following the number. In case the compound is unsaturated, the above rules apply except that number one (1) is used as the fourth last digit.

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TABLE 3  
SUMMARY OF THE PRODUCT DISTRIBUTION FOR THE  
ELECTROCHEMICAL FLUORINATION OF  
TRICHLOROETHYLENE

Run No.	1	2	3	4	5*
Cell Current, A Start-Final	13.7-0.6	12.8-0.4	15.7-0.9	10.5-0.6	2.0-1.0
Reaction Time, hr	54.0	46.1	52.0	50.0	48.0
Product Distribution, mole percent					
$\text{CHCl}_2\text{-CCl}_2$ (F-1120)	63.4	77.3	47.0	63.3	71.2
$\text{CHCl}_2\text{-CCl}_2\text{F}$ (F-121)	13.0	8.4	15.6	11.0	5.7
$\text{CHCl}_2\text{-CClF}_2$ (F-122) + $\text{CHClF-CCl}_2\text{F}$ (F-122a)	20.2	12.8	31.4	22.6	17.8
$\text{CCl}_2\text{F-CClF}_2$ (F-113)	3.4	1.5	6.0	3.1	5.3
Current Passed, A-hr	79.4	52.0	94.4	74.1	56.5
Current Efficiency, %	33.2	32.0	41.4	37.2	43.4

\*Hydrogen fluoride preelectrolyzed for a period of 32.1 A-hrs.

The total current efficiency was calculated based upon one electron transferred for each fluorine atom added to the products listed in Table 3. The current efficiencies and the product distribution for all runs including that where AHF was pretreated electrochemically are quite consistent. Current efficiencies ranged from 32.0 to 43.4%. The highest current efficiency was achieved when hydrogen fluoride was pretreated to remove any water content. Lower current efficiencies observed during the other cases most likely resulted from the electrolysis of impurities in AHF such as water at the beginning of the run. The major product formed in all runs was the doubly fluorinated compound representing approximately 21 to 47 mole percent of the products, followed by the singly and triply fluorinated compounds as listed in Table 3. The consistent results can be attributed to the accurate temperature and voltage control of this process. In this investigation no attempt was made to collect any gaseous products that could have formed from carbon-carbon scission or from higher degrees of fluorination. The triply fluorinated compound never exceeded 6 mole percent; therefore, it seemed unlikely that much highly fluorinated material was produced.

Figure 6 shows the major two-carbon-chain products of the electrochemical fluorination of trichloroethylene as a function of reaction time while Figure 7 gives the product distribution as a function of the ampere-hours applied for a typical run. The increasing slope of the product lines in Figure 7 indicates

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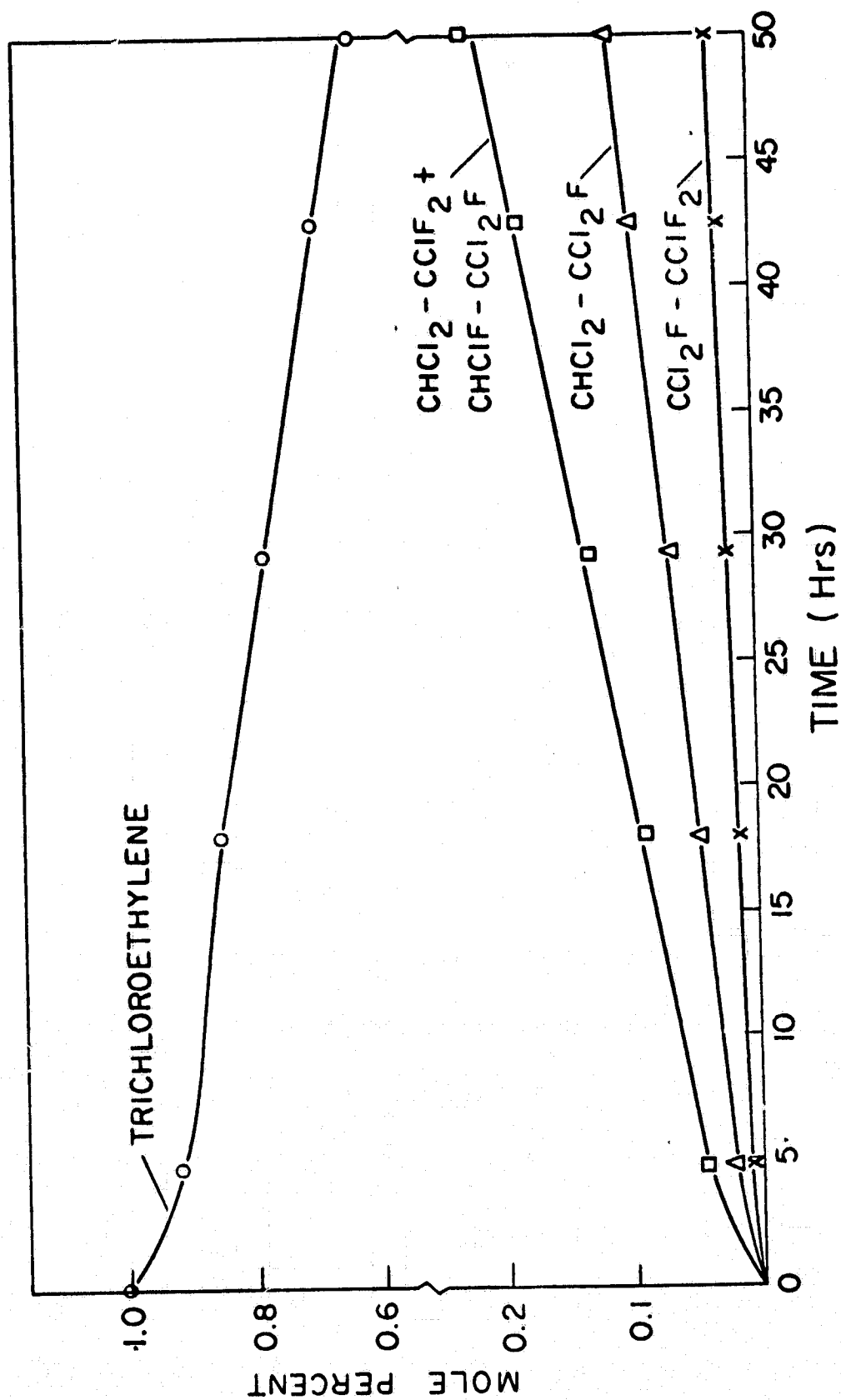


Fig. 6 Typical Product Distribution as a Function of Reaction Time,  
Operated at a Constant Cell Voltage

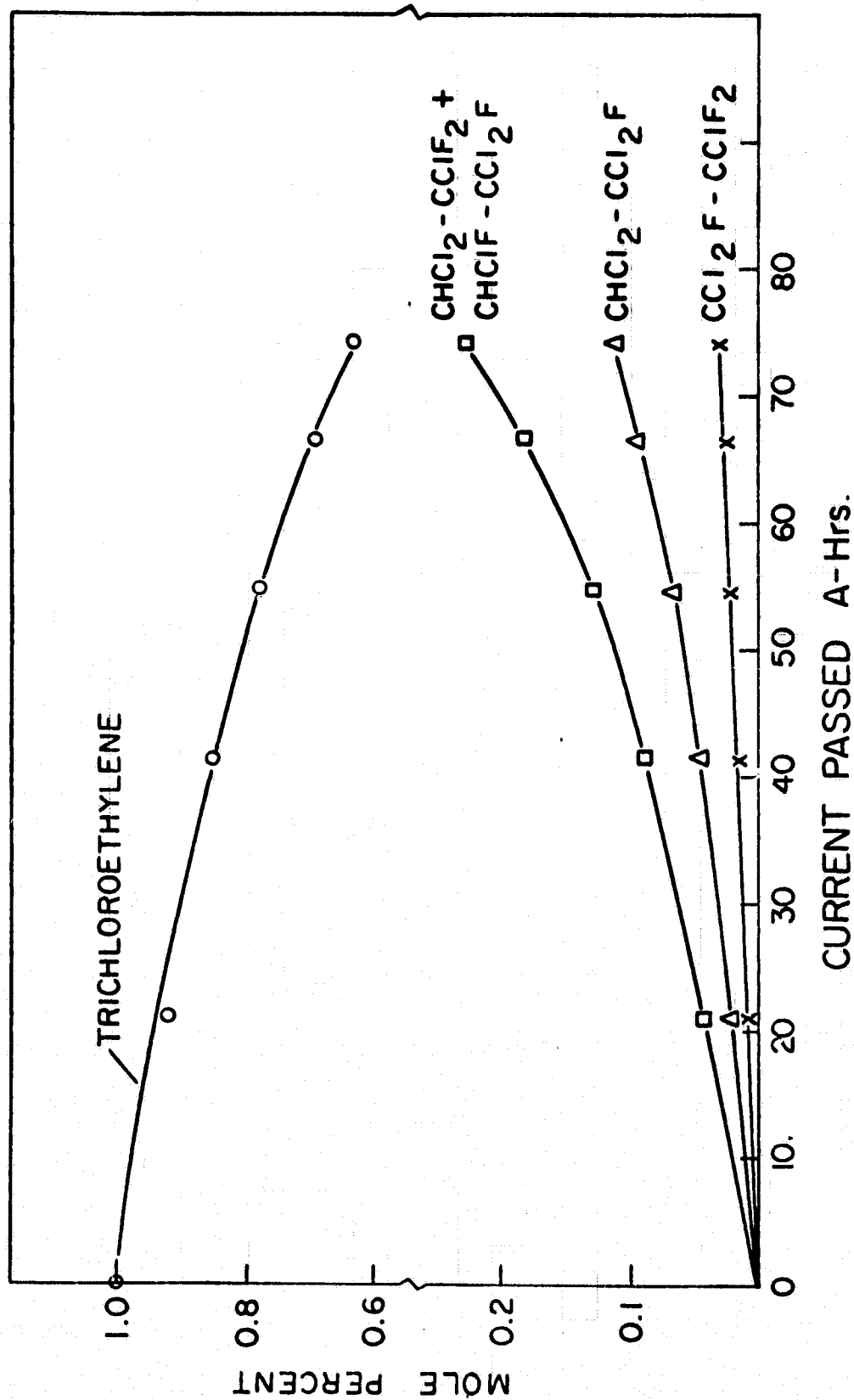


Fig. 7 Typical Product Distribution as a Function of Current Passed,  
Operated at a Constant Cell Voltage



that the current efficiency increased as the reaction proceeded. This trend was not observed during the run featuring the pre-electrolysis period which showed a fairly constant current efficiency throughout the duration of the experiment. Cell current as a function of reaction time for a typical run is shown in Figure 8. The cell current decreased quickly from an initial current of 10.5 amperes to less than 2 amperes after five hours. Trichloroethylene is not ionizable in AHF; hence, once the water in the AHF was electrochemically removed, the solution became a poor conductor resulting in a decrease in the cell current under a constant voltage mode of operation.

Drakesmith and Hughes (11) report in their study of the electrochemical fluorination of propene in AHF at about 0°C, that the chemical addition of hydrogen fluoride to the double bond occurs. In a comparison experiment, 222 g of trichloroethylene was added to 258 g of AHF under operating conditions identical to those of Table 1, but without applying any power. This run was carried out for 20.2 hours and the products were analyzed. No fluorinated compounds were observed, indicating that chemical fluorination of trichloroethylene did not take place under these experimental conditions. Chemical fluorination of trichloroethylene with hydrogen fluoride had been reported to be accomplished, but at much higher temperatures, i.e. 200°C (46,47, 48).

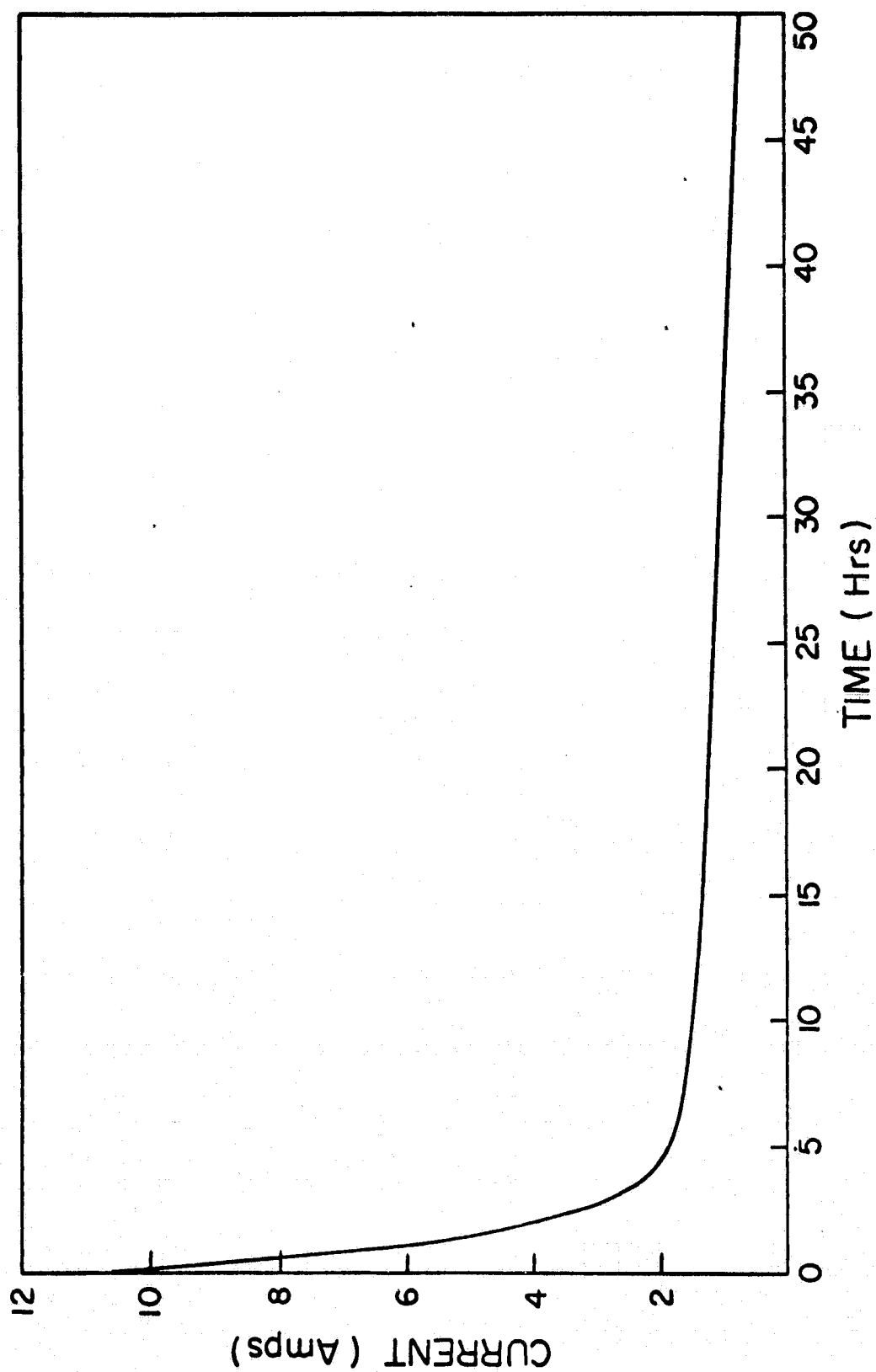
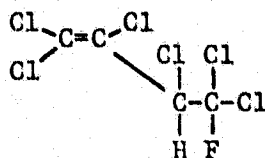
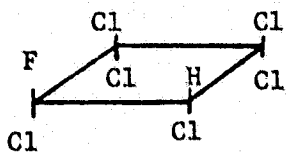


Fig. 8 Cell Current as a Function of Reaction Time for a Typical Trichloroethylene Run, Operated at a Constant Cell Voltage

Figure 9 shows a typical gas chromatographic analysis of the products in this study. This analysis identifies the groups of compounds listed in Table 3. Calibration runs using available standards of F-121, F-122 and F-113 confirm the presence of these components in the product mixture.

A more in-depth analysis of a sample selected from one of the runs involved the use of GC-MS, proton n.m.r. and  $^{19}\text{F}$  n.m.r. One must realize that the cost involved in all these analyses for each sample was extremely high; consequently, only a detailed analysis for a selected run can be undertaken. It is believed that the results of the analysis of this specific run should be representative of all the runs under similar experimental conditions. In this study, run 1 was chosen for detailed analysis. Further details of the analytical work can be found in the Appendix. The combined GC-MS analysis of the product mixture indicated that the  $\text{C}_2\text{HCl}_3\text{F}_2$  peak in the GC analysis included a mixture of the isomers F-122 and F-122a. Furthermore, the GC-MS analysis revealed that a compound having the formula  $\text{C}_4\text{HCl}_6\text{F}$  was present in the product mixture. This compound was observed at a retention time outside of the range of the chromatogram shown in Figure 9. Based on the GC-MS and n.m.r. analyses, an unsaturated or ring structure was postulated for this compound. Possible structures are shown below:



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1. 1,1,2-TRICHLOROTRIFLUOROETHANE
2. 1,1,2-TRICHLORO-2,2-DIFLUOROETHANE
3. 1,1,2-TRICHLORO-1,2-DIFLUOROETHANE
4. TRICHLOROETHYLENE
5. 1,1,2,2-TETRACHLOROFUOROETHANE

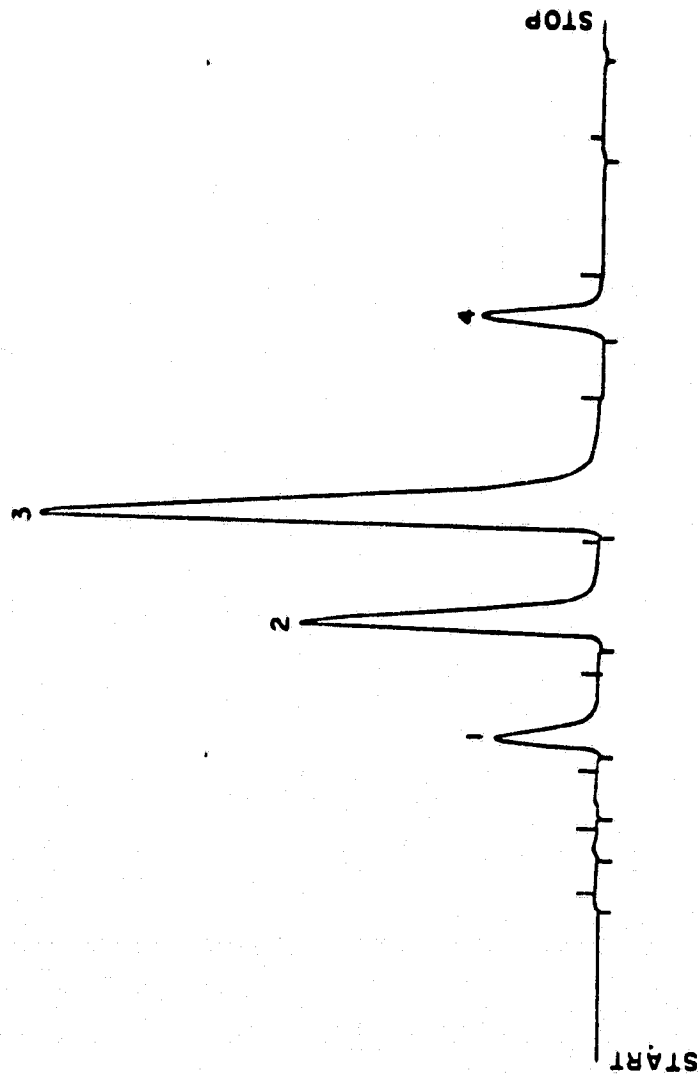


Fig. 9 Typical Gas Chromatographic Analysis

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A quantitative determination of the product distribution was obtained from the GC and n.m.r. analyses, and the results are presented in Table 4. Again, there is no reason to believe that the product distributions for the other runs would differ considerably from the results of this one. The consideration of  $C_4HCl_6F$  would result in higher current efficiencies than those reported in Table 3. The GC-MS analysis also indicated the presence of minute quantities of several other compounds; they are listed in Table 5.

TABLE 4

DETAILED PRODUCT DISTRIBUTION FOR THE  
ELECTROCHEMICAL FLUORINATION OF  
TRICHLOROETHYLENE

<u>Freon Code No.</u>	<u>Compound</u>	<u>Mole Percent</u>
F-1120	$CHCl=CCl_2$	50.2
F-121	$CHCl_2-CCl_2F$	10.3
F-122	$CHCl_2-CClF_2$	2.6
F-122a	$CHClF-CCl_2F$	13.4
F-113	$CCl_2F-CClF_2$	2.7
F-C-321/F-1321	$C_4HCl_6F$	13.7
	Others	7.1

TABLE 5

MINOR PRODUCTS FROM THE ELECTROCHEMICAL  
FLUORINATION OF TRICHLOROETHYLENE

<u>Freon Code No.</u>	<u>Compound</u>
F-111	$\text{CClF}=\text{CCl}_2$
F-1110	$\text{CCl}_2=\text{CCl}_2$
F-114a	$\text{CCl}_2\text{F}-\text{CF}_3$
F-114	$\text{CClF}_2-\text{CClF}_2$
F-112	$\text{CCl}_2\text{F}-\text{CCl}_2\text{F}$
F-112a	$\text{CCl}_3-\text{CClF}_2$
	other high molecular weight chloro-fluoro compounds

In order to examine closely the products obtained in this investigation, a comparison of the products of chemical and electrochemical fluorinations by other investigators would be beneficial. Hauptschein and Bigelow (49) reported that the vapor phase reaction of trichloroethylene with fluorine produced the major products of 1,1,2-trichlorotrifluoroethane (F-113) and 1,1,2,2-tetrachlorodifluoroethane (F-112). The vapor phase fluorination of trichloroethylene with cobalt trifluoride and manganese trifluoride was investigated by Fuller et al. (50). The product distribution for this work is shown in Table 6. The products of these chemical fluorinations of trichloroethylene and

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those reported by Hsu, Schmidt and Schmidt, Wolfe and this investigation are summarized in Table 7. The products reported in this work closely resemble those obtained by Fuller et al. using either metal fluoride as the reactant and those products obtained by Hauptschein and Bigelow. The major products of this study, F-121, F-122a and F-113 were also reported as major products in both of the above cases. Of the minor reaction products observed in our study, F-112 and F-114 were also reported in the chemical fluorination runs (49,50).

TABLE 6

SUMMARY OF THE PRODUCT DISTRIBUTION FOR THE  
VAPOR PHASE FLUORINATION OF TRICHLOROETHYLENE  
BY FULLER ET AL.

<u>Freon Code No.</u>	<u>Compound</u>	<u>Mole Percent</u>	
		<u>CoF<sub>3</sub> Reagent</u>	<u>MnF<sub>3</sub> Reagent</u>
F-114 + F-133a	CClF <sub>2</sub> -CClF <sub>2</sub> + CH <sub>2</sub> ClCF <sub>3</sub>	18.8	0
F-123a, F-123b	C <sub>2</sub> HCl <sub>2</sub> F <sub>3</sub>	9.6	7.1
F-113	CCl <sub>2</sub> F-CClF <sub>2</sub>	45.2	13.4
F-122a	CHClF-CCl <sub>2</sub> F	8.5	54.9
F-112	CCl <sub>2</sub> F-CCl <sub>2</sub> F	17.9	0
F-121, F-121a	C <sub>2</sub> HCl <sub>4</sub> F	0	24.6

Burdon and Tatlow (26) state that the products of reaction with elementary fluorine are similar to those of electrochemical

TABLE 7  
PRODUCTS OF CHEMICAL AND ELECTROCHEMICAL  
FLUORINATIONS

Freon Code No.	Formula	Boiling Pt. °C	Reference Where Products Observed
F-112	$\text{CCl}_2\text{F}-\text{CCl}_2\text{F}$	92.8	B, W, F, P
F-112a	$\text{CCl}_3-\text{CClF}_2$	91.5	P
F-113*	$\text{CCl}_2\text{F}-\text{CClF}_2$	47.6	B, W, H, F, P
F-114	$\text{CClF}_2-\text{CClF}_2$	3.6	W, H, F, P
F-114a	$\text{CCl}_2\text{F}-\text{CF}_3$	3.0	P
F-121*	$\text{CHCl}_2-\text{CCl}_2\text{F}$	116.6	W, F, P
F-121a	$\text{CHClF}-\text{CCl}_3$	116.5	F
F-122*	$\text{CHCl}_2-\text{CClF}_2$	71.9	H, P
F-122a*	$\text{CHClF}-\text{CCl}_2\text{F}$	72.6	W, H, S, F, P
F-123a	$\text{CHClF}-\text{CClF}_2$	28.2	F
F-123b	$\text{CHF}_2\text{CCl}_2\text{F}$		F
F-131	$\text{CHCl}_2-\text{CHClF}$	102.5	H
F-131a	$\text{CH}_2\text{Cl}-\text{CCl}_2\text{F}$	88.5	
F-133a	$\text{CF}_3-\text{CH}_2\text{Cl}$	6.1	F
F-1110	$\text{CCl}_2=\text{CCl}_2$	120.8	P
F-1111	$\text{CClF}-\text{CCl}_2$	71.0	P
F-C-321/ F-1321*	$\text{C}_4\text{HCl}_6\text{F}$		P

Reference Code:

B	Hauptschein and Bigelow (1950)	chemical
F	Fuller, et al. (1962)	chemical
H	Hsu (1979)	electrochemical
S	Schmidt and Schmidt (1953)	electrochemical
W	Wolfe (1952)	electrochemical
P	This paper	electrochemical

\*Indicates major products found in this work



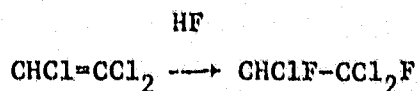
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fluorination; however, the products from reactions involving high-valency metal fluorides do not resemble those of electrochemical fluorinations. The products reported in this work resemble those obtained from reaction with both elementary fluorine and high-valency metal fluorides. This observation is significant since it indicates that the chemical and electrochemical fluorination of trichloroethylene occur by similar mechanisms.

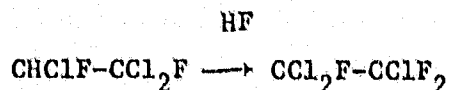
The electrochemical fluorination of trichloroethylene in a solution of hydrogen fluoride and acetonitrile was investigated by Schmidt and Schmidt (15) and resulted in simple addition of fluorine to the double bond to give  $\text{CHClF}-\text{CCl}_2\text{F}$  (F-122a) as the principal product.

One of the objectives in this investigation was to establish the reaction path for the electrochemical fluorination of trichloroethylene under experimental conditions similar to those of Wolfe and Hsu. Wolfe (13) postulated that in the fluorination of trichloroethylene by electrolysis in liquid AHF at about  $0^\circ\text{C}$  and at a constant voltage of 6.0 volts, the following stepwise reactions are involved;

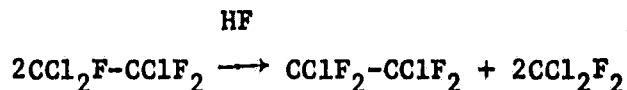
Step 1. Addition of fluorine to the double bond



Step 2. Replacement of hydrogen with fluorine



Step 3. Further fluorination reactions and decomposition



The product distribution obtained with vigorous agitation of the cell contents was 82 percent  $\text{CHClF}-\text{CCl}_2\text{F}$  (F-122a), 12 percent  $\text{CCl}_2\text{F}-\text{CClF}_2$  (F-113) and 6 percent other material. Other major products observed for operation between 5 and 8 volts were  $\text{CHCl}_2-\text{CCl}_2\text{F}$  (F-121) and  $\text{CCl}_2\text{F}-\text{CCl}_2\text{F}$  (F-112). Current efficiencies between 80 and 90% were reported.

More recently, Hsu proposed an alternate reaction mechanism for the same process. The prospective reaction products, assuming no rearrangement or chlorination reactions, and their boiling points are shown in Figure 10. The product distribution reported by Hsu for a run conducted at 0°C and 7.5-15 volts is shown in Figure 11; the product distribution for a run at 5-10°C and 6 volts is shown in Figure 12. Based on these experimental results, Hsu stated that the initial fluorination step is the homolytic (anti-Markovnikov) addition of hydrogen fluoride to the double bond rather than fluorine addition. This step is followed by replacement of hydrogen resulting in the formation of primarily 1,1,2-trichloro-2,2-difluoroethane (F-122) instead of its isomer 1,1,2-trichloro-1,2-difluoroethane (F-122a) as reported by Wolfe and Schmidt and Schmidt.

Based upon the products obtained in this study, a reaction path for the electrochemical fluorination of trichloroethylene is

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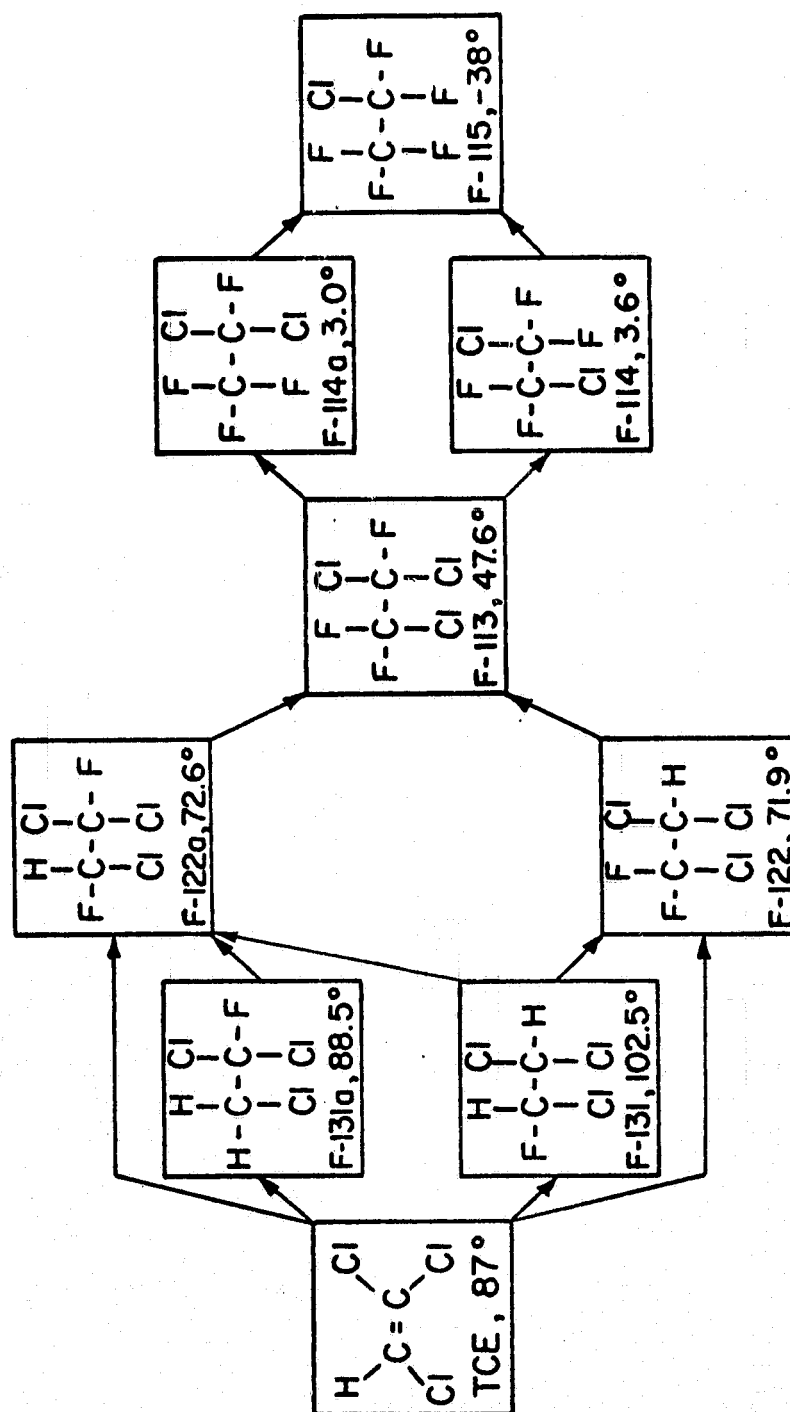


Fig. 10 Prospective Reaction Products and their Boiling Points of the  
Electrochemical Fluorination of Trichloroethylene

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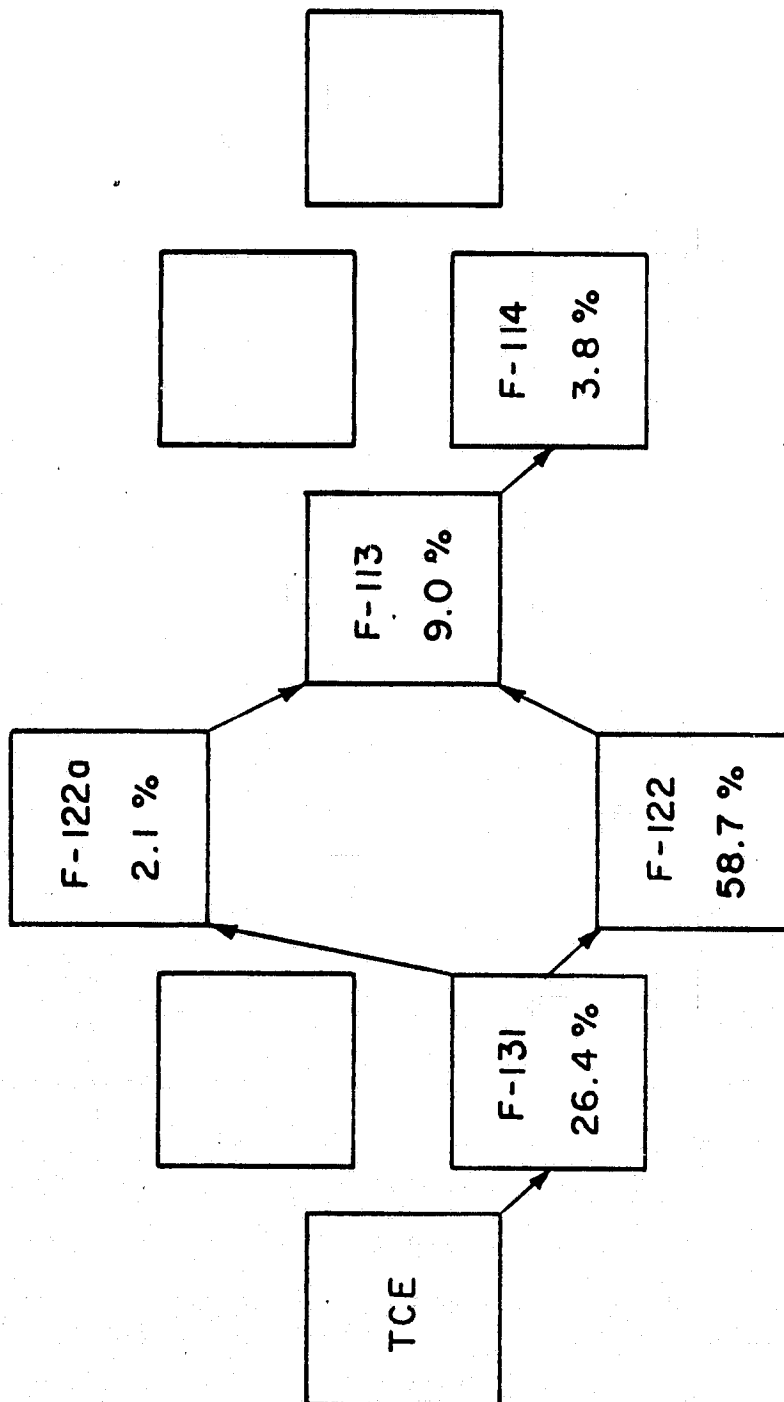


Fig. 11 Product Distribution (Mole Percents) of the Electrochemical Fluorination of Trichloroethylene at 0°C and 7.5-15V, According to Hsu (9)

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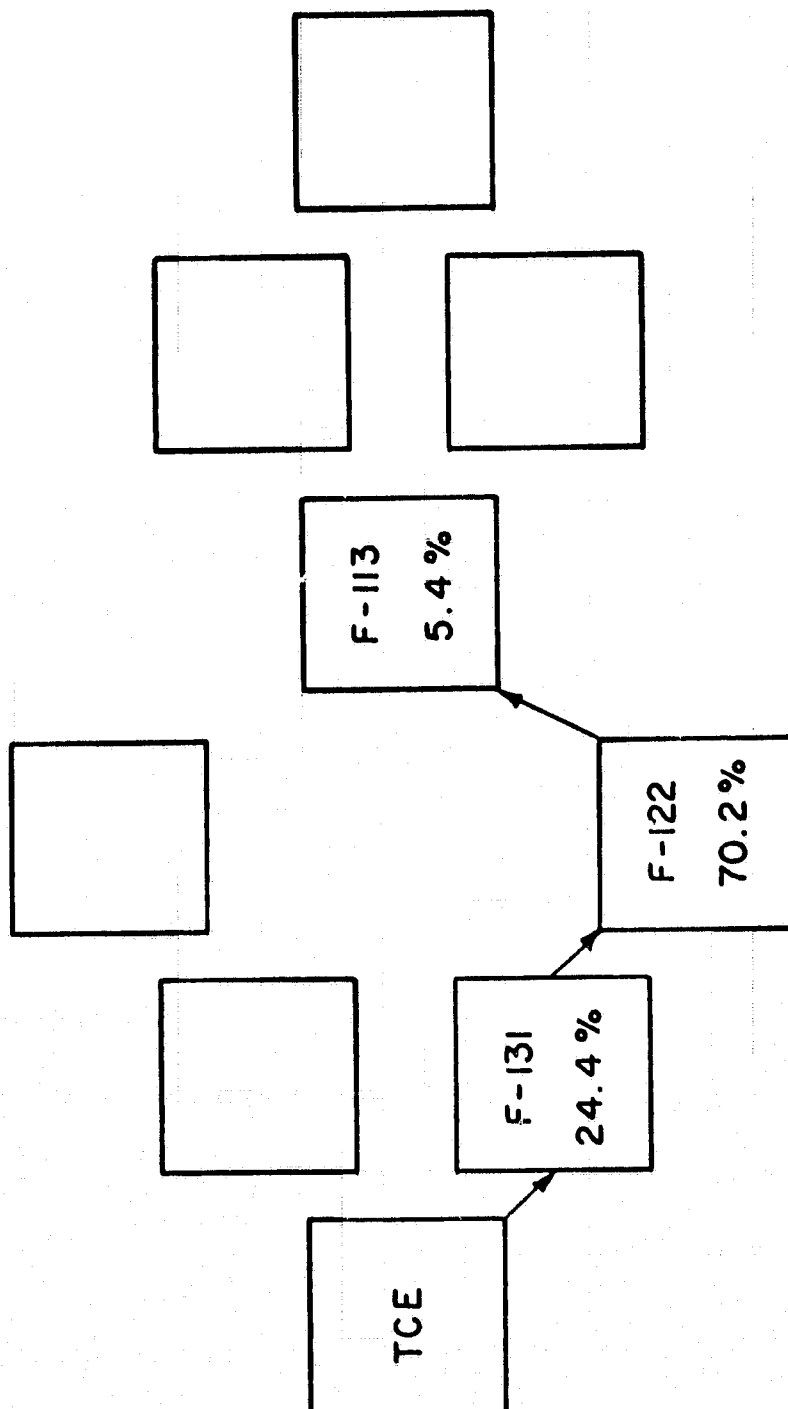


Fig. 12 Product Distribution (Mole Percents) of the  
Electrochemical Fluorination of Trichloroethylene  
at 5-10°C and 6V, According to Hsu (9)

presented in Figure 13. Generally, in electrochemical fluorinations of chlorohydrocarbons, hydrogen rather than chlorine tends to be replaced first by fluorine. This phenomenon was also observed in this study. The postulated reaction path is in close agreement with that proposed by Wolfe. An interesting reaction product was 1,1,2,2-tetrachlorofluoroethane (F-121) which consists of four chlorine atoms, one more than in the initial reactant, trichloroethylene. This product was also observed by Wolfe and Fuller et al. No sign of the singly fluorinated product, 1,1,2-trichloro-2-fluoroethane (F-131), as reported by Hsu, was observed in this work or in any other works cited here. Hsu used only gas chromatography to analyze his product mixtures. It is very likely that Hsu produced F-121, but labeled it F-131 as a result of their high boiling points. Again Hsu may have produced mostly F-122a instead of the reported F-122, based on their close boiling points. The small quantity of F-122a claimed by Hsu may actually have been trichlorofluoroethane (F-1111).

Chemical fluorination with elementary fluorine or high-valency metal fluorides is considered a free-radical type process (26). Thus, based on this study and analogies with chemical fluorination, the electrochemical fluorination of trichloroethylene is also considered an anodic free-radical type reaction. This statement can be further substantiated by the fact that the three main products of the high temperature chemical fluorination of trichloroethylene,  $\text{CH}_2\text{ClCCl}_2\text{F}$ ,  $\text{CH}_2\text{ClCClF}_2$  and  $\text{CH}_2\text{ClCF}_3$  (46,47,48),

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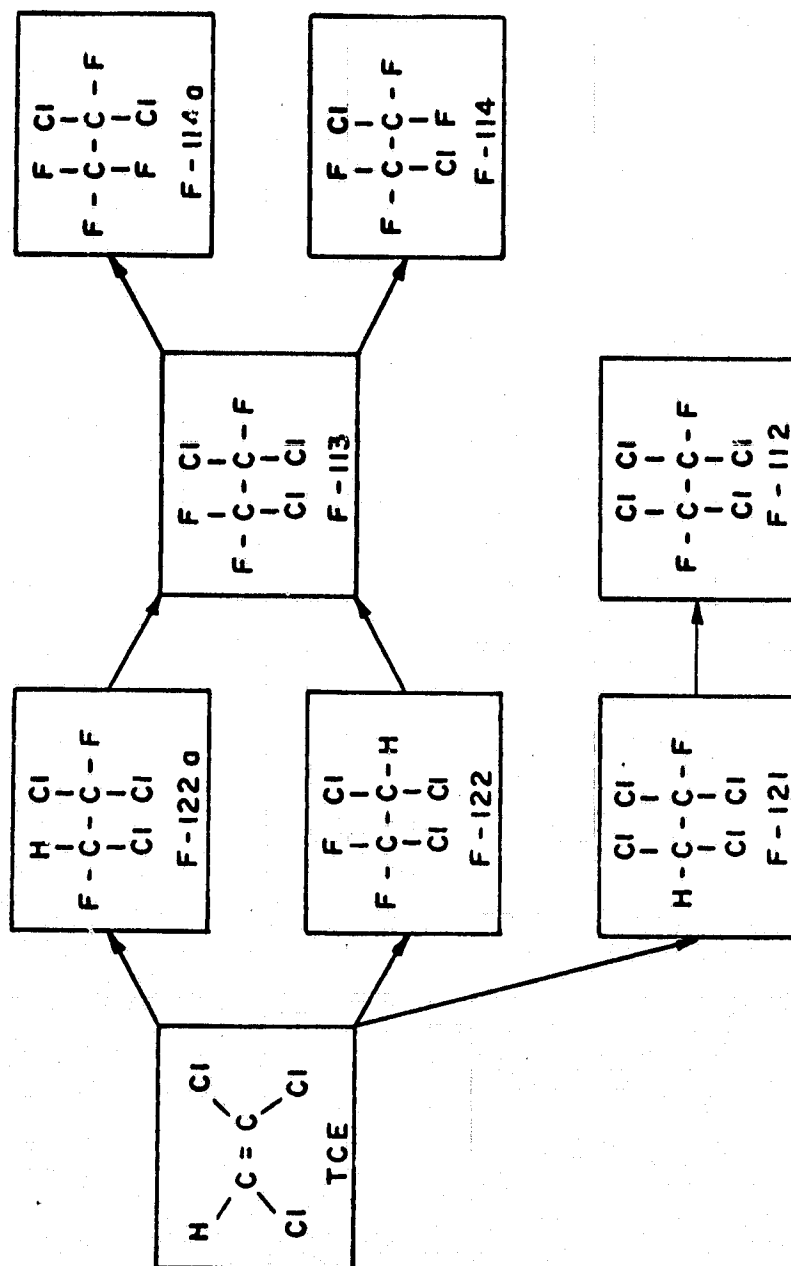


Fig. 13 Postulated Reaction Path for the Electrochemical  
Fluorination of Trichloroethylene

formed by ionic reactions, were not observed in this or in other electrochemical fluorination studies of trichloroethylene.

The results of this work indicate that the fluorine radical formed from the electrochemical reaction combines chemically with trichloroethylene forming either of two intermediate free radicals as shown in Figure 14. These radicals can then react chemically with fluorine, chlorine or hydrogen to produce the additional products shown in Figure 14. Of these products, F-121 and F-122a were observed in this work. F-122a can be produced from either of the free radical intermediates; however, F-121 would require the formation of the less stable intermediate,  $\text{CCl}_2\text{F}-\text{CHCl}^\bullet$ . It would be expected that a mixture of the two intermediates would be formed, resulting in a mixture of the isomers F-121 and F-121a; however, F-121a was not observed. Products formed by reaction of hydrogen with the intermediate (F-131, F-131a) were not observed. Possibly, the free radical can more easily extract a fluorine or chlorine atom from another molecule due to their greater availability in comparison to the hydrogen atom. The formation of F-122 cannot be explained by this mechanism; however, it was present in much lower concentrations than its isomer F-122a. Replacement of hydrogen and subsequently chlorine in the compounds shown in Figure 14 would lead to many of the other observed products.

Polymerization can occur from reaction of trichloroethylene and a free radical intermediate; for example:



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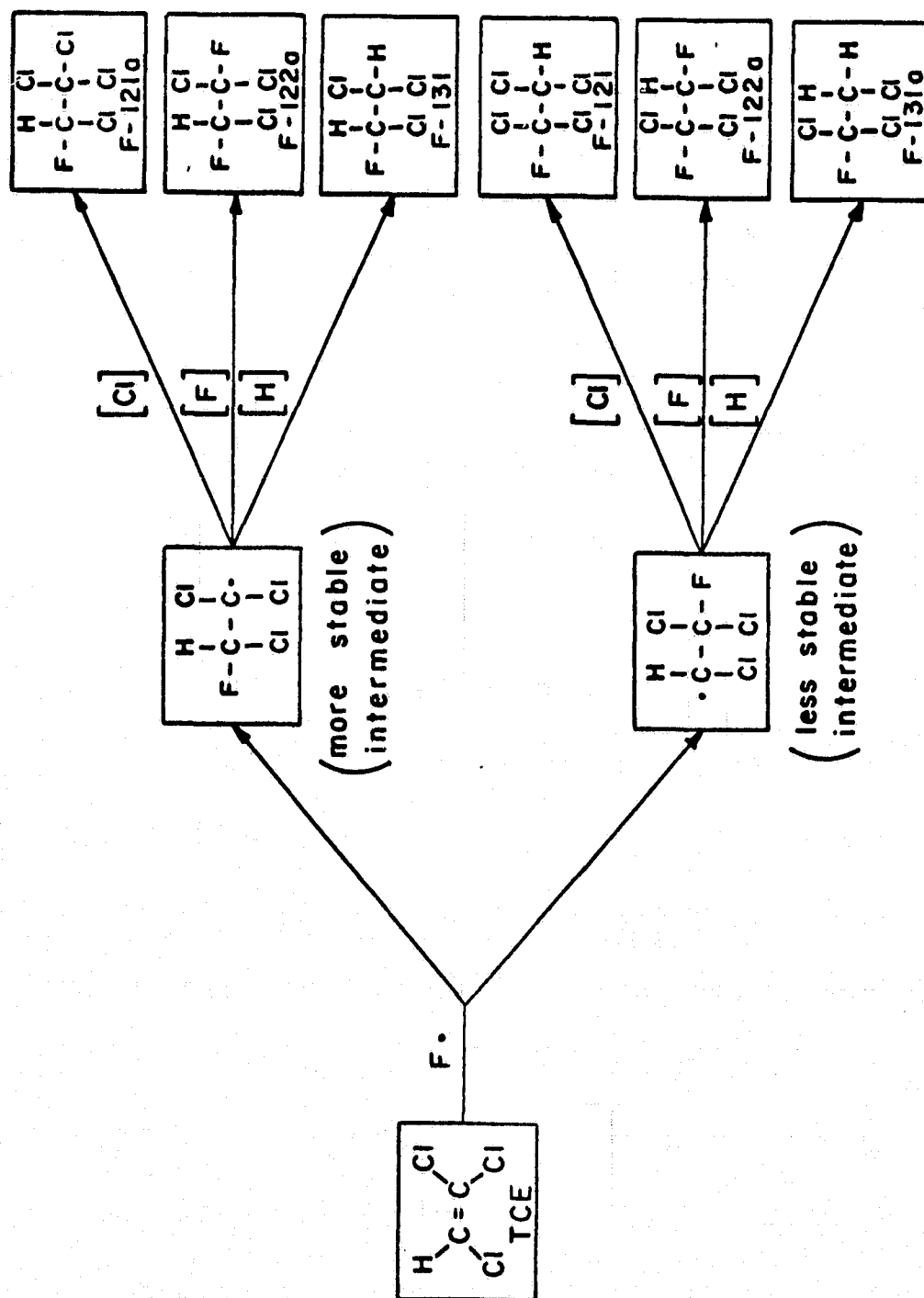
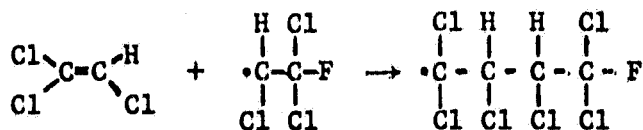


Fig. 14 Postulated Reaction Mechanism for the Electrochemical Fluorination of Trichloroethylene



This free radical can then react with fluorine or chlorine or combine with trichloroethylene or another free radical to form C<sub>6</sub>, C<sub>8</sub> or higher molecular weight compounds. Cyclic compounds can also be formed from these free radical reactions. Additional substitution of hydrogen and chlorine by fluorine can also potentially lead to a wide variety of products.

#### 4.2 The Electrochemical Fluorination of Solid Polymeric Materials

##### 4.2.1 Solid Substrates Added Directly to the Reactor

The results of the electrochemical fluorination of solid polymeric materials added directly to the reactor are summarized and presented in Table 8. Six runs were conducted in this study. A single run was carried out with a polyvinyl alcohol (PVA) substrate and three runs were conducted with a polyacrylic acid (PAA) substrate. A comparison run with PAA was performed without power to determine if any chemical fluorination occurs. In addition, a run without substrate was tried to investigate the effect of the substrate on the conductivity of the solution.

The relative fluorine to carbon ratio was determined by the electron spectroscopy for chemical analysis (E.S.C.A.) technique. One must note that the accuracy of E.S.C.A. for elemental analysis is not better than ±30 percent. Further discussion on the E.S.C.A.

TABLE 8

SUMMARY OF RESULTS OF THE ELECTROCHEMICAL FLUORINATION  
OF SOLID POLYMERIC MATERIALS

Run No.	Solid Polymer	Solid Weight, g	AHF Volume, ml	"Fluorinert" Volume, ml	Current Range, A	Reaction Time, hrs	Current Passed, A-hr	Relative F/C Ratio (Based on Sample #2-b)
1	Polyvinyl Alcohol	1.1	325	75	16.6-0.88	21.6	51.4	10.4
2 <sup>†</sup>	Polyacrylic Acid	6.0	125	275	14.0-0.49	21.1	38.2	a) 3.7 b) 1
3	Polyacrylic Acid	2.0	150	200	19.2-0.19	23.3	36.9	3.6
4	Polyacrylic Acid	2.0	325	75	20.2-0.92	21.1	59.9	2.2
5*	Polyacrylic Acid	2.0	325	75	-	22.7	-	3.0
6	-	-	325	75	20.8-0.41	21.2	44.1	-
7	Polyacrylic Acid (Anode Coating)	0.62	450	0	0.10-0.48	7.1	2.0	0.40
8	Polyacrylic Acid (Anode Coating)	6.0	450	0	-	8.5	-	0.32

\*Refrigeration unit failed; average temperature was 13°C

<sup>†</sup>Two samples taken

results is given in appendix 4. The greatest degree of fluorination was observed with the PVA substrate; however, only a small amount of the starting material could be recovered as product. Products from the other runs were recovered as either thin films on the cathode plates or as a large rubbery mass found on the reactor bottom or impeller blades. Two samples were taken in Run 2. The sample removed from the cathode plates (a) showed a higher level of fluorination than the majority of the product, which was recovered as a large rubbery ball-shaped product on the reactor bottom. This was expected since the rubbery compound was not well mixed with the AHF reactant. A comparison of runs 4 and 5 shows that a higher degree of fluorination occurred during the run without power. This was not expected; however, the experimental error involved in E.S.C.A. and in selecting a representative sample may account for this phenomena.

Nevertheless, it can be rationalized that the chemical fluorination of PAA does occur. The assessment of the chemical fluorination of PVA was not undertaken in this study, thus no comparison could be made to the electrochemical fluorination of PVA.

High initial currents were observed during these runs; however, the current drops off exponentially to less than 2 amps after 5 hours. Cell current as a function of reaction time for a typical run is presented in Figure 15. Run 6, conducted with no substrate, also shows high currents. The average current for

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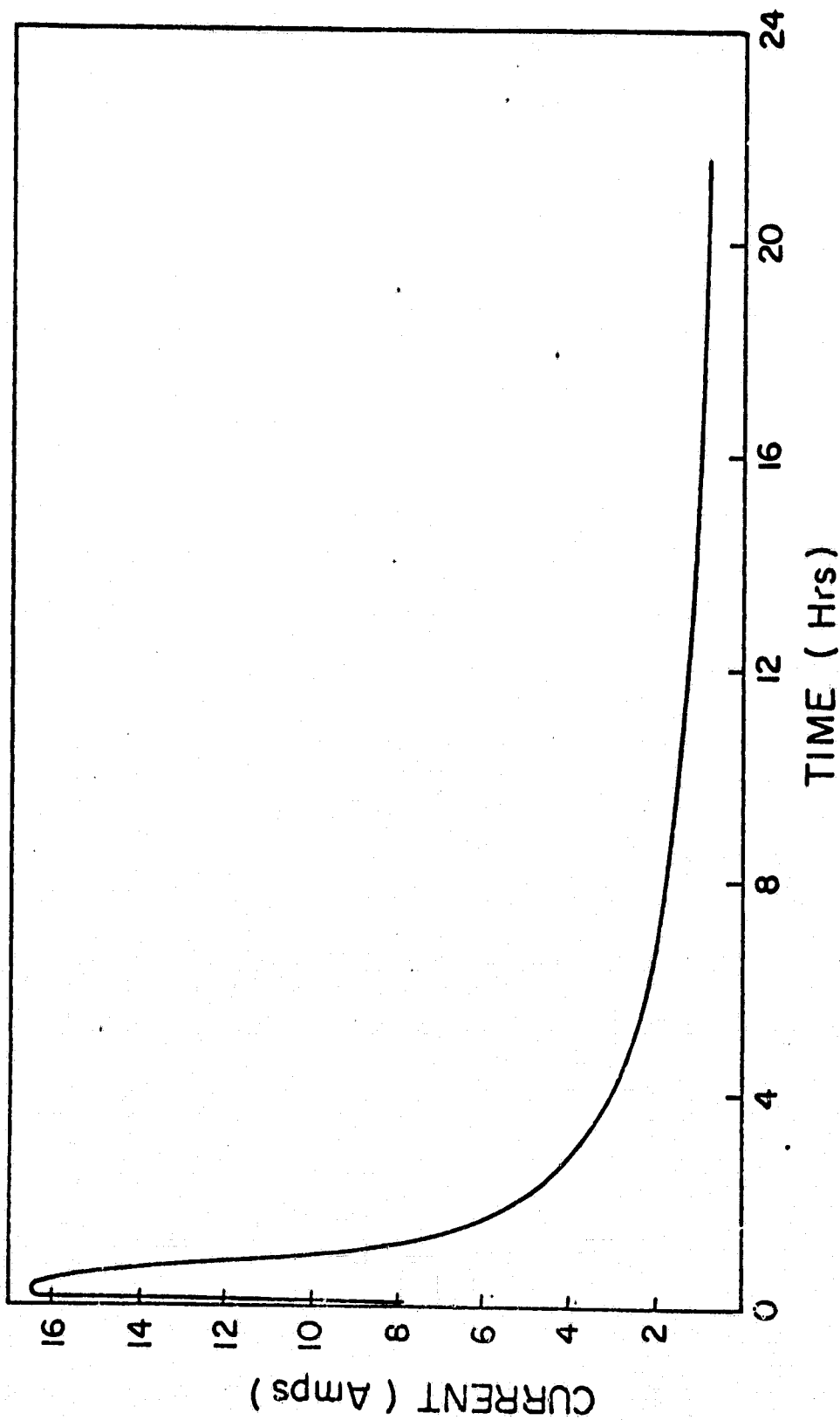


Fig. 15 Cell Current as a Function of Reaction Time for a  
Typical Solid Polymer Run, Operated at a Constant  
Cell Voltage

run 6, 2.1 amps, is only slightly less than that of run 4, 2.8 amps. Consequently, it suggests that the substrate does not contribute significantly to the conductivity of the solution.

"Fluorinert" is a highly nonconductive liquid. The greater proportion of "Fluorinert" in run 3 yielded a lower average current of 1.6 amps. The high currents observed in these runs most likely resulted from the electrolysis of impurities in the AHF.

#### 4.2.2 Solid Substrates Coated on the Anode

Two runs were conducted with the polyacrylic substrate coated directly on the anode surface; they are also summarized and included in Table 8. For comparison, run 8 was conducted without power. A PAA film was pressed onto the polymer coating in this run. The polymers had been radiation crosslinked in both runs. Most of the coating separated from the anode surface upon contact with the AHF and remained between the electrodes, but did not dissolve.

The relative fluorine to carbon ratio differs only slightly between the two runs. This seems to indicate that only chemical fluorination of the PAA took place. Possibly the separation of the polymer from the anode surface allowed the current to bypass the membrane. A much lower degree of fluorination was found in these runs in comparison to those where the solid substrate was added directly to the reactor. The poor mass transfer characteristics of the anode coating tests, due to lack of mixing, probably account for the low degree of fluorination.

#### 4.2.3 Chemical Stability of Crosslinked Versus Non-Crosslinked Solid Polymeric Materials

The chemical resistance to AHF of the solid polymer films was tested. Four samples, crosslinked PVA and PAA, and non-crosslinked PVA and PAA, were immersed in AHF at 0°C for about 12 hours. The films ranged in thickness from 0.3 to 0.5 mm. Both samples of PAA retained their shape and showed negligible weight loss. The samples remained clear and showed a slight gray color. The crosslinked PVA film softened and turned a dark amber color while the non-crosslinked PVA film dissolved to form a thick amber-colored liquid. Therefore, it appears that radiation crosslinking was somewhat effective in improving the chemical stability of the PVA film.

## 5. CONCLUSIONS AND RECOMMENDATIONS

### 5.1 The Electrochemical Fluorination of Trichloroethylene

A microprocessor aided electrochemical fluorination system has been constructed and used to obtain highly reproducible experimental results for the electrochemical fluorination of trichloroethylene. The current efficiency for production of two-carbon-chain products is approximately 30-40%, assuming one electron transfer for each fluorine addition. The following major two-carbon-chain products were observed under the conditions of this study, i.e., 0°C operating temperature and 6.0V:  $\text{CHCl}_2\text{-CCl}_2\text{F}$ ,  $\text{CHCl}_2\text{-CClF}_2$ ,  $\text{CHClF-CCl}_2\text{F}$  and  $\text{CCl}_2\text{F-CClF}_2$ . With respect to the reaction type and its pathway, the electrochemical fluorination of trichloroethylene is almost certainly an anodic free-radical reaction. The first step in the reaction sequence was determined to be fluorine addition to the double bond, followed by replacement of first hydrogen and then chlorine by fluorine. Chlorination reactions took place in this process producing tetrachloro compounds. Also polymerization among trichloroethylene and free-radical intermediates yielded higher molecular weight and possibly ring type chlorofluorohydrocarbons.

Several recommendations can be made to improve the accuracy of the experimental results and help elucidate the mechanism of



the electrochemical fluorination process, The use of conductivity additives and a lower substrate concentration will lead to a greater degree of fluorination or a shorter reaction time. A better sampling system on the reactor should be devised so that smaller volume samples can be taken to assure that any variation of the experimental conditions would be minimized. If a greater degree of fluorination is achieved, the liquid nitrogen cold traps should be used to collect the highly fluorinated products.

A more accurate analysis of the product mixture can be obtained with the aid of a fractional distillation. The information on the temperatures corresponding to the various fractions will help identify the unknown compounds.

Interaction among the products and reactants can complicate the determination of the reaction path. It is suggested that a careful study of the time dependence of the products early in the reaction be carried out.

It appears as though most reported work with applied potential has been performed with a controlled cell voltage. Therefore, the IR losses in the electrolyte and cathodic overpotential cannot be expected to be the same nor reproducible among different investigators. It is advised that experiments be conducted with controlled anodic potential using a high current potentiostat to obtain data independent of the IR drop and events occurring at the cathode.

## 5.2 The Electrochemical Fluorination of Solid Polymeric Materials

A preliminary investigation into the fluorination of polyvinyl alcohol and polyacrylic acid did not show any conclusive evidence that an electrochemical fluorination reaction took place. Similar degrees of fluorination occurred in experiments with PAA conducted either with or without power. The chemical fluorination of PAA was observed to occur by simply immersing the film into AHF. Only relative fluorine to carbon ratios were determined in these studies. Radiation crosslinking was found to improve the chemical stability of PVA films in AHF. Both crosslinked and non-crosslinked PAA films were stable in the AHF.

Additional experiments should be carried out to determine if the chemical fluorination of PVA occurs in AHF. A more detailed chemical analysis of the solid polymeric products should be undertaken to determine the sites on the molecule where the fluorination takes place. Also the actual fluorine to carbon ratio instead of a relative ratio should be obtained. Analyzing a fluorocarbon standard using the E.S.C.A. technique may yield this result.

A new reactor should be constructed that would incorporate the membrane as a cell separator and divide the cell into an anode and cathode compartment. This would allow for a more positive test for the electrochemical fluorination of the membrane.

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# APPENDIX 1. GAS CHROMATOGRAPHY ANALYSIS

A quantitative analysis of the reaction products of the electrochemical fluorination of trichloroethylene was performed using a Hewlett Packard 5840A gas chromatograph. The column used was 254 cm of 0.32 cm diameter stainless steel packed with 20% SP-2100, 0.1% Carbowax 1500 on 100/120 mesh Supelcoport. A helium flowrate of 20 ml/min was used in this column as well as in a reference column. The gas chromatograph was operated under the following conditions:

oven temperature	125°C
injection temperature	200°C
thermal conductivity detector temperature	175°C

A 5  $\mu$ l sample size was usually used.

The standard compounds used in the gas chromatographic analysis are listed in Table A1.

TABLE A1

## STANDARD COMPOUNDS USED IN THE GAS CHROMATOGRAPHIC ANALYSIS

<u>Freon Code No.</u>	<u>Compound</u>	<u>Vendor</u>
F-113	$\text{CCl}_2\text{F}-\text{CClF}_2$	Pfaltz and Bauer
F-121	$\text{CHCl}_2-\text{CCl}_2\text{F}$	Columbia Organic
F-122	$\text{CHCl}_2-\text{CClF}_2$	Columbia Organic
F-131	$\text{CHCl}_2-\text{CHClF}$	Accurate Chemical and Scientific
F-1110	$\text{CCl}_2=\text{CCl}_2$	Fisher Scientific

A typical chromatogram, including retention times in minutes, is shown in Figure A1. The column used in this analysis tends to separate the components by boiling points. When the product solution was mixed with standards of F-113, F-121 and F-122 no new peaks emerged on the chromatogram. This indicates that these compounds or compounds boiling very close to them were present. Products solutions mixed with F-131 and F-1110 resulted in additional peaks on the chromatogram.

1. 1,1,2-TRICHLOROTRIFLUOROETHANE
2. 1,1,2-TRICHLORO-2,2-DIFLUOROETHANE
3. 1,1,2-TRICHLORO-1,2-DIFLUOROETHANE
4. 1,1,2,2-TETRACHLOROETHYLENE

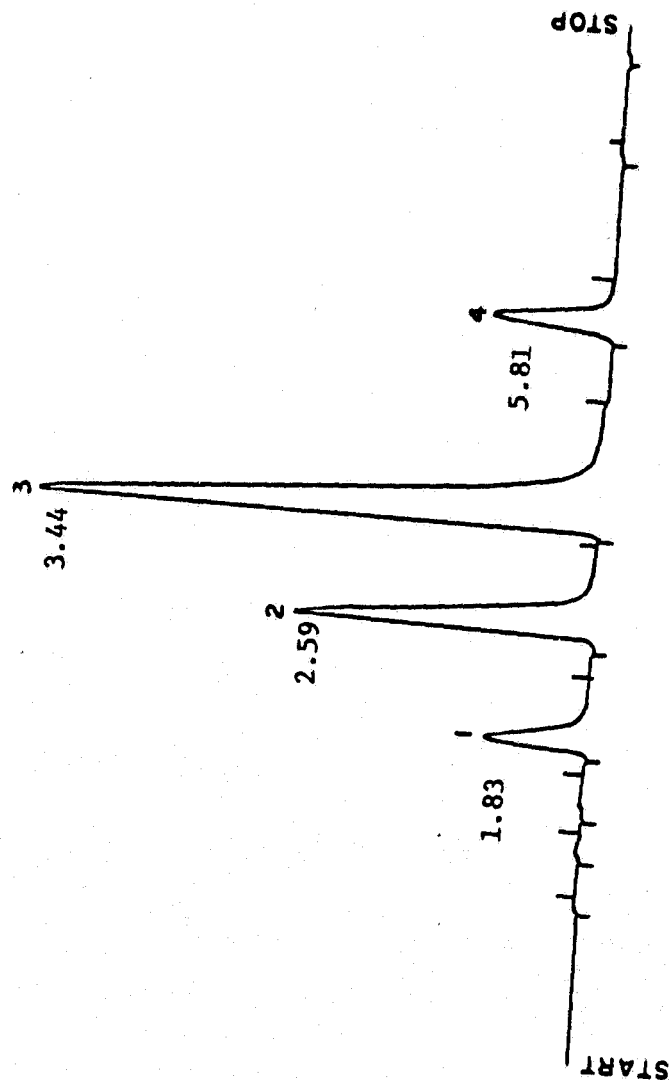


Fig. A1 Typical Gas Chromatographic Analysis,  
Including Retention Time in Minutes



## APPENDIX 2. GAS CHROMATOGRAPHY-MASS SPECTROMETRY ANALYSIS

A GC-MS analysis of a product sample from a selected run of the electrochemical fluorination of trichloroethylene was accomplished with a coupled Varian-MAT-CH-7 mass spectrometer and a Varian 1740 gas chromatograph. Plots were generated on a Varian SS-200 Data System. The purpose of this analysis was to determine the presence of any other compounds that may have been located under the GC peaks. Close boiling compounds may not be resolved under simple GC analysis. No attempt was made with the GC-MS analysis to quantify the amounts of the reaction products.

The same column described in the GC analysis was used in addition to a 3% SP-2100 column. The oven temperature was held at 25°C for 5 minutes and then increased to 135°C at a rate of 10°C/min. The helium gas flow rate was 30 ml/min.

The first column resulted in a better separation. The chromatogram, using this column, has four major peaks and is shown in Figure A2. This chromatogram is similar to the one presented earlier in Figure A1. Mass spectrometry revealed the presence of the low boiling isomers F-114 and F-114a in a small peak at the beginning of the GC output. The F-1111 boils very close to F-122 and F-122a, and was located within the second major peak shown in Figure A2. Both F-112 and F-112a were observed under the third major peak, trichloroethylene. These compounds

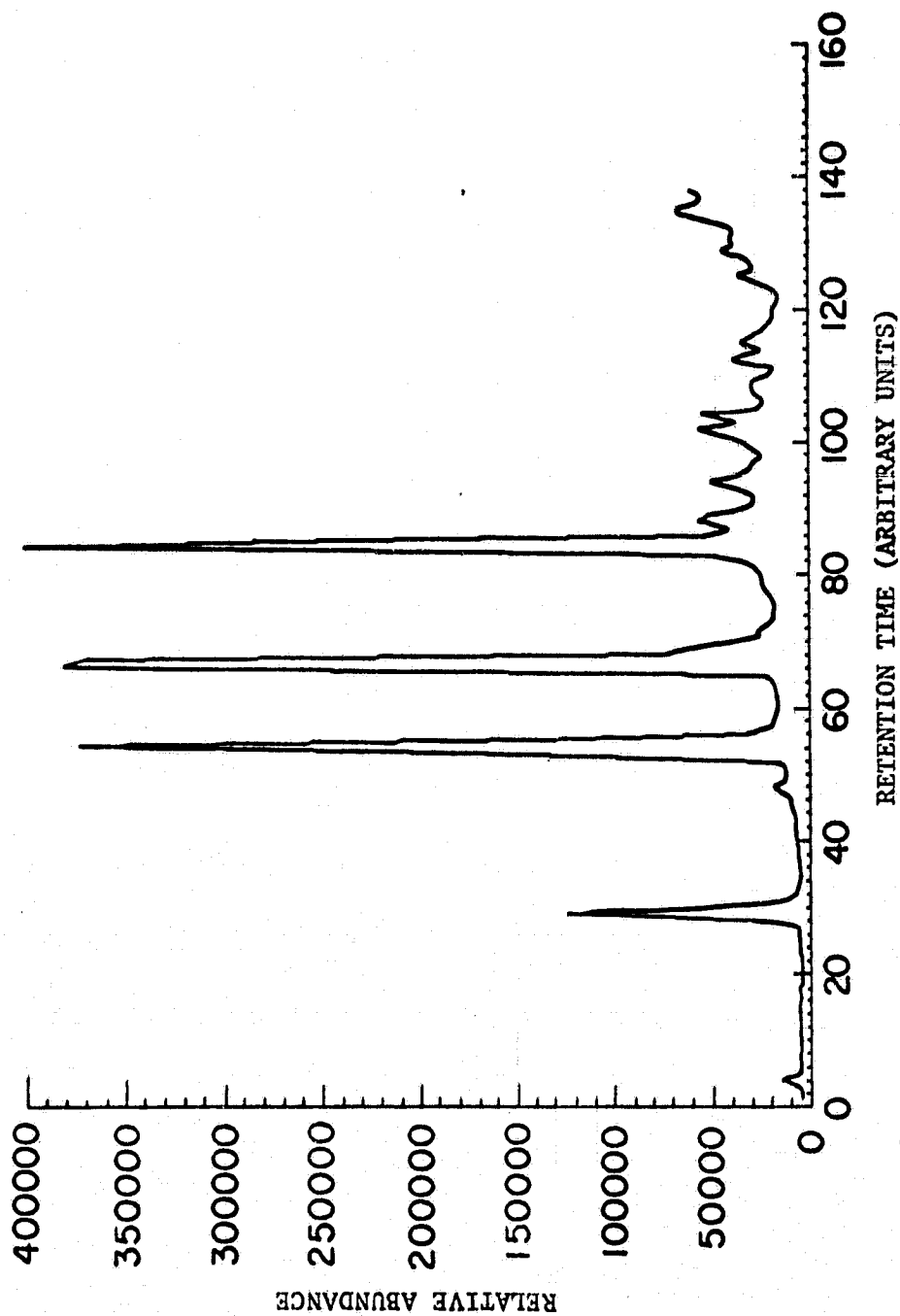
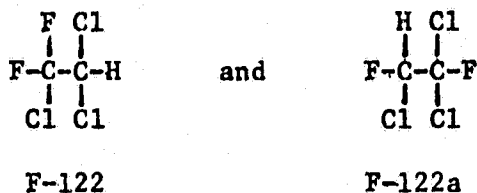


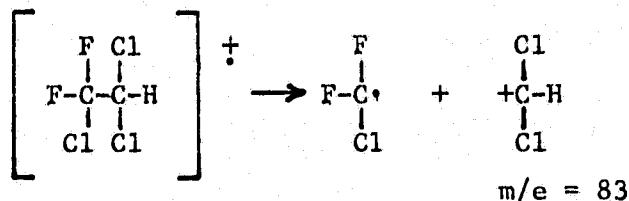
Fig. A2 Chromatogram From the GC-MS Analysis

are solids at room temperature; however, standards were found to be soluble to at least 14 weight percent in the product solution. The F-1110 was observed under the fourth major peak. Only a very small amount of this compound can be present since the product solution mixed with a standard of F-1110 revealed an additional peak in the GC analysis. The  $C_4HCl_6F$  compound and higher molecular weight chloro-fluoro compounds were observed in MS scans of the higher retention time peaks.

A typical example of the analysis of the MS spectra is described below. The MS scans of the second major peak, positions 53 and 54 of the chromatogram, are shown in Figures A3 and A4, respectively. These spectra differ considerably and indicate a mixture of the isomers:



A standard spectrum of F-122 is shown in Figure A5. The radical cation of F-122 can undergo fragmentation to form the peak at the m/e (mass to charge ratio) value of 83:



The peak at 168 corresponds to the molecular weight of F-122, while the peak at 133 indicates loss of a chlorine atom (molecular

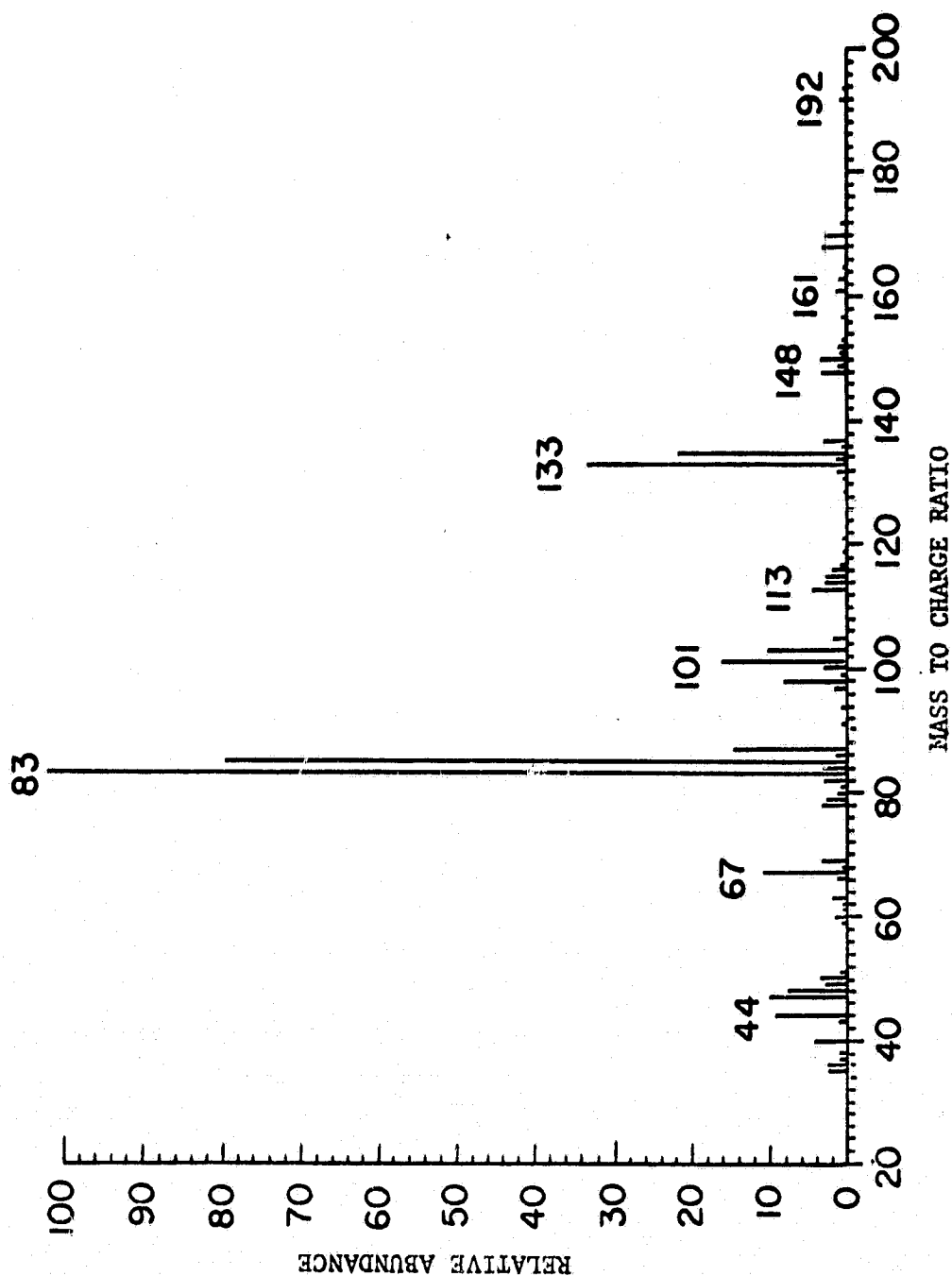


Fig. A3 Mass Spectrum of Retention Time 53 of the  
GC Analysis Shown in Figure A2

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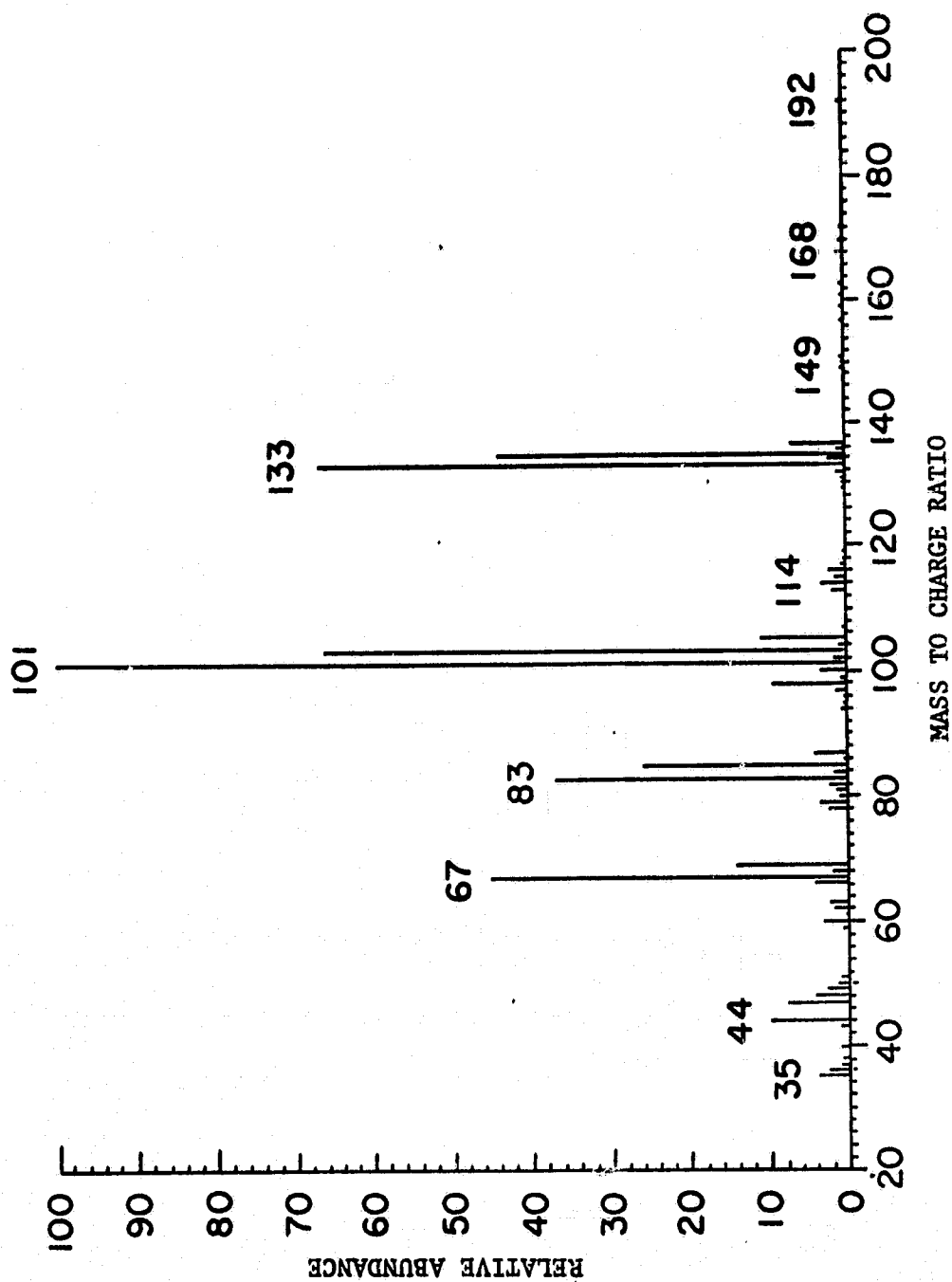


Fig. A4 Mass Spectrum of Retention Time 54 of the  
GC Analysis Shown in Figure A2

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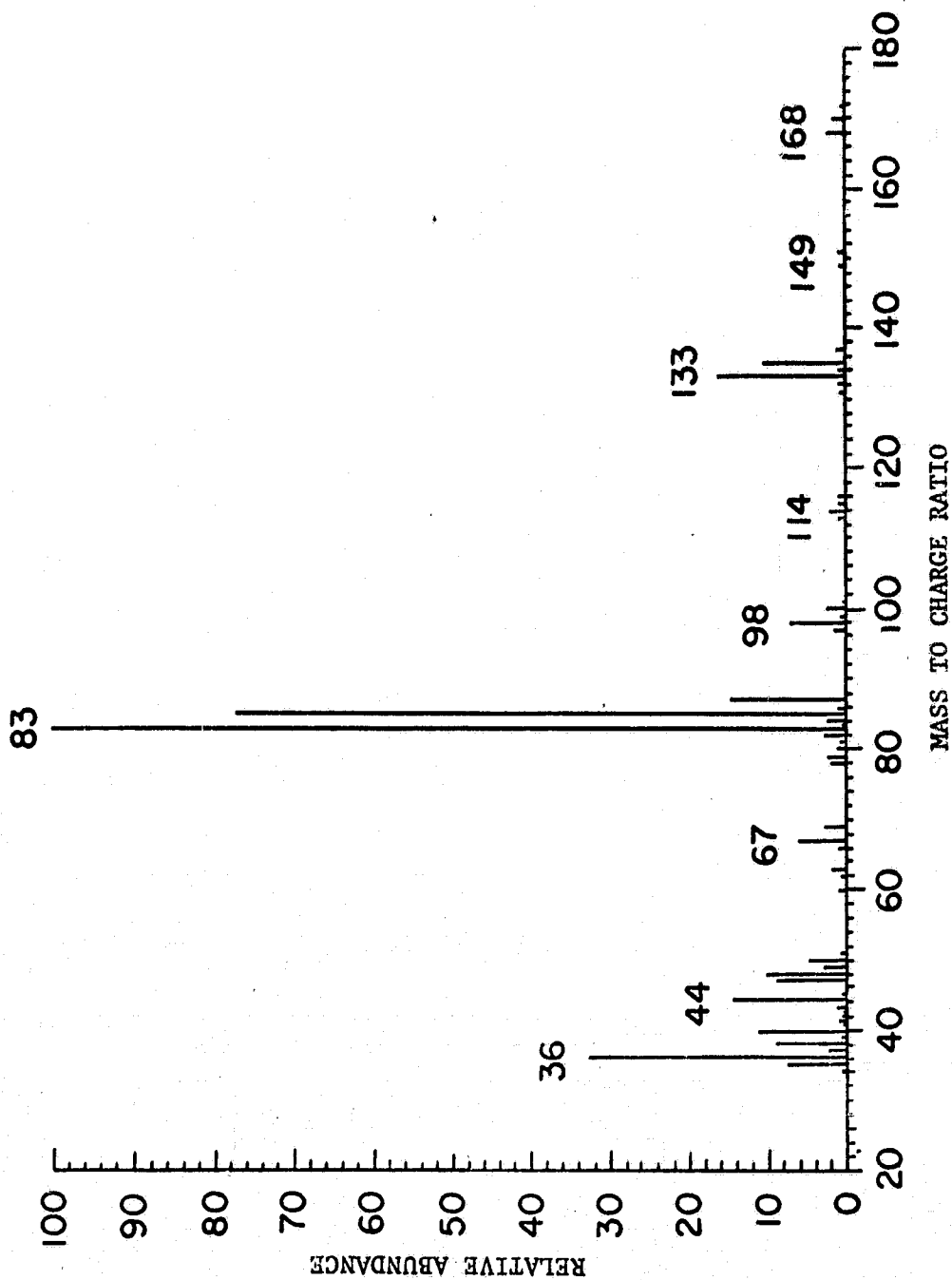
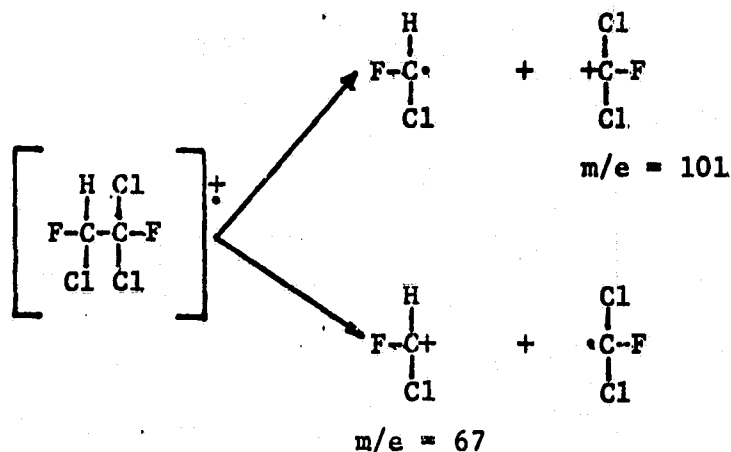


Fig. A5 Mass Spectrum of 1,1,2-Trichloro-2,2,-difluoroethane  
(F-122)

weight of 35) from the molecule. The peaks at 83, 133, and 168 were all observed in Figures A3 and A4. However, major peaks at  $m/e$  values of 101 and 67 were also found in these spectra. These peaks can arise from the fragmentation reactions of the F-122a radical cation:



The spectra at the retention time positions of 53 and 54 showed greater proportions of F-122 and F-122a, respectively. This is reasonable since F-122a has a slightly higher boiling point.

The peak at 148 could be due to  $\text{CClF}=\text{CCl}_2$  (F-1111) since it corresponds to the molecular weight of the compound. The presence of the other compounds listed in Table 5 were all determined from a similar study of the fragmentation reactions.

APPENDIX 3. PROTON AND  $^{19}\text{F}$  N.M.R. ANALYSIS

A more in-depth analysis of the reaction products of the electrochemical fluorination of trichloroethylene was accomplished with proton and  $^{19}\text{F}$  n.m.r.  $^{19}\text{F}$  n.m.r. was performed with a Varian XL-100 n.m.r. spectrometer. Proton n.m.r. was accomplished with a Varian XL-200 n.m.r. spectrometer. The n.m.r. analysis was used to quantitatively determine the amounts of the doubly fluorinated isomers, the  $\text{C}_4\text{HCl}_6\text{F}$  polymer and other compounds. Only the total of the isomers, F-121 and F-121a, could be found from the GC analysis. Also, it was difficult to determine the amount of  $\text{C}_4\text{HCl}_6\text{F}$  present from the GC analysis due to the absence of a calibration standard. In addition, the n.m.r. analysis allowed some insight into the structure of the  $\text{C}_4\text{HCl}_6\text{F}$  compound.

Proton and  $^{19}\text{F}$  n.m.r. spectra are shown in Figures A6 and A7, respectively. Relative areas, chemical shifts, coupling constants and probable identity of the peaks are listed in Tables A2 and A3. Standards of trichloroethylene, F-113, F-121 and F-122 were used to identify several of the peak sets in the spectra. Relative areas in both spectra were based on a value of 100 for F-121.

Christie and Pavluth (A1) reported, in their  $^{19}\text{F}$  n.m.r. analysis of F-122a, a doublet of doublets at -69.6 ppm (relative to  $\text{CFCl}_3$ ) with vicinal H-F and F-F coupling constants of 3.5



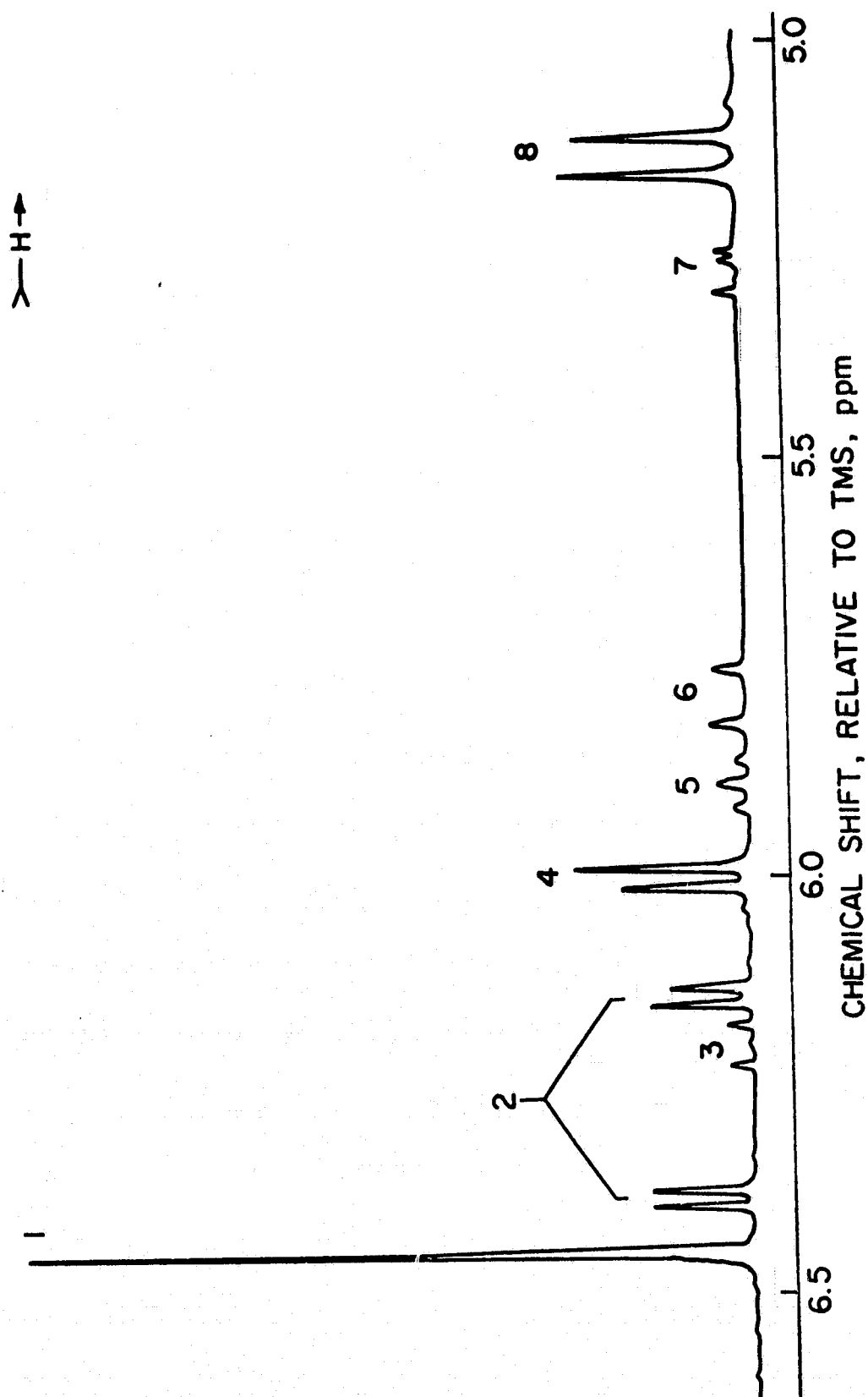


Fig. A6 Proton N.M.R. Spectrum

TABLE A2

## DETAILS OF PROTON N.M.R. SPECTRUM

Peak Set No.	Peak Type	Chemical Shift, ppm (Relative to TMS)	Coupling Constants, Hz	Relative Areas	Compound
1	singlet	6.45	0	209.9	CHCl=CCl <sub>2</sub>
2	doublet of doublets	6.26	3.9, 48.3	125.6	CHClF-CCl <sub>2</sub> F (F-122a)
3	doublet	6.21	10.0	15.5	-
4	doublet	6.00	4.5	100.0	CHCl <sub>2</sub> -CCl <sub>2</sub> F (F-121)
5	triplet	5.89	5.5	24.8	CHCl <sub>2</sub> -CClF <sub>2</sub> (F-122)
6	doublet	5.78	13.0	27.7	-
7	-	-	-	23.0	-
8	doublet	5.14	8.9	128.5	C <sub>4</sub> HCl <sub>6</sub> F

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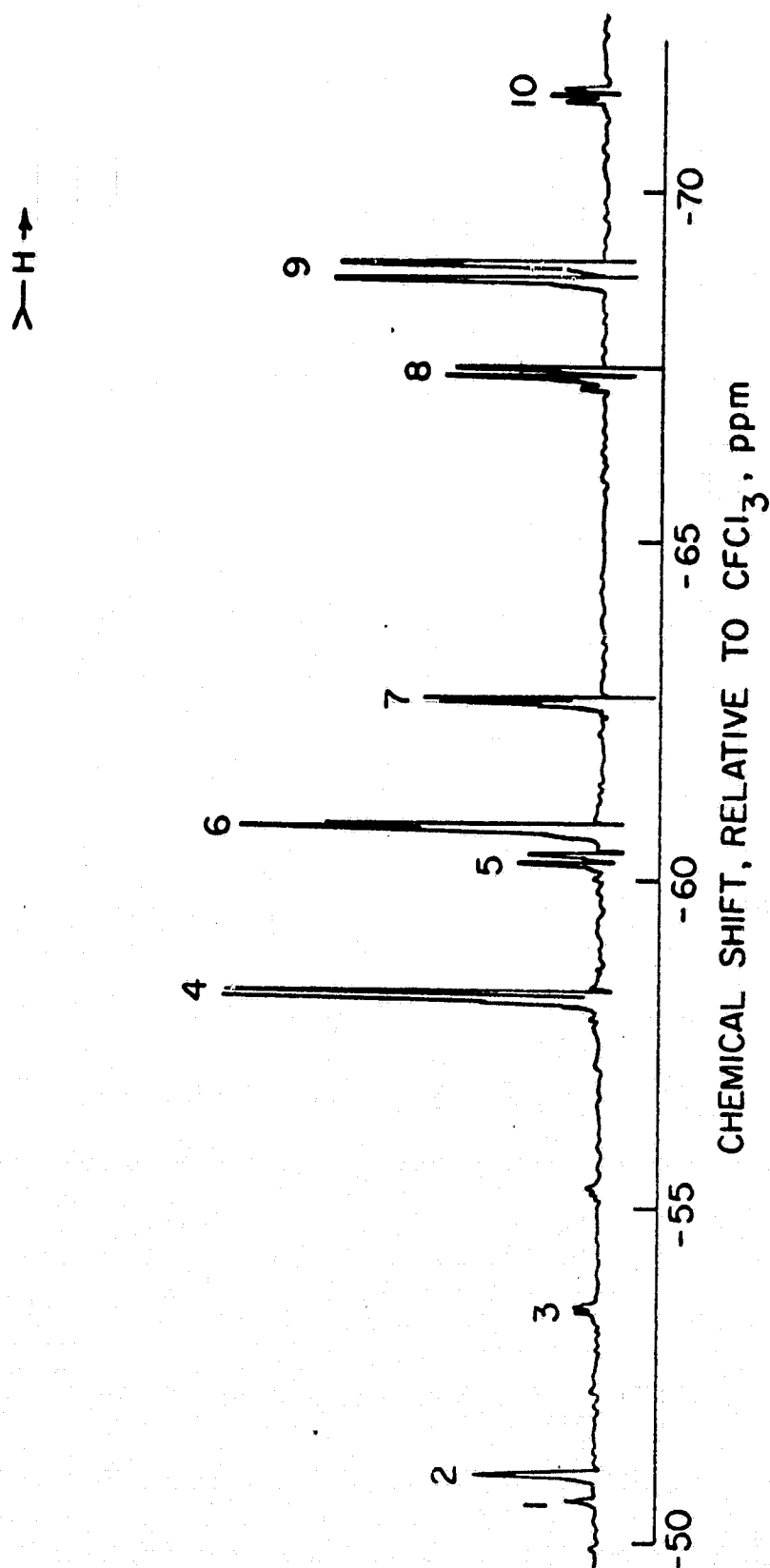


Fig. A7  $^{19}\text{F}$  N.M.R. Spectrum

TABLE A3  
DETAILS OF  $^{19}\text{F}$  N.M.R. SPECTRUM

Peak Set No.	Peak Type	Chemical Shift, ppm (Relative to $\text{CFCl}_3$ )	Coupling Constants, Hz	Relative Areas	Compound
1	doublet	-50.6	4.5	5.8	-
2	singlet	-51.0	0	25.4	-
3	doublet	-53.5	6.2	8.0	-
4	doublet	-58.2	8.7	115.6	$\text{C}_4\text{HCl}_6\text{F}$
5	doublet	-60.2	13.0	28.8	-
6	doublet	-60.6	4.7	100.0	$\text{CHCl}_2\text{-CCl}_2\text{F}$ (F-121)
7	doublet	-62.5	6.2	38.6	$\text{CHCl}_2\text{-CClF}_2$ (F-122)
8	doublet	-67.4	9.6	46.2	$\text{CCl}_2\text{F-CClF}^*$ (F-113)
9	doublet of doublets	-68.9	3.6, 24.5	108.0	$\text{CHClF-CCl}_2\text{F}^*$ (F-122a)
10	triplet	-71.4	9.6	19.7	$\text{CCl}_2\text{F}^*\text{-CClF}_2$ (F-113)

\*Indicates fluorine associated with peak

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and 24 Hz respectively. They also reported a proton n.m.r. spectrum featuring a doublet of doublets at 6.61 ppm (relative to TMS) with vicinal H-F and geminal H-F coupling constants of 3.5 and 47 Hz, respectively. Peak set 2 of the proton spectrum and peak set 9 of the  $^{19}\text{F}$  spectrum can be attributed to F-122a since their coupling constants agree very closely with these values, although the chemical shifts show some disagreement. An additional doublet of doublets, with coupling constants of 24 and 47 Hz, corresponding to the fluorine on the protonated carbon of F-122a would be expected on the  $^{19}\text{F}$  spectrum. These peaks were not reported by Christie and Pavluth and were not observed in the spectrum of Figure A7. This doublet of doublets would probably appear further upfield and outside the range of the above spectrum. For example, a similar fluorine in  $\text{CHClF-CHClF}$  resonates at a chemical shift of -174 ppm (A2).

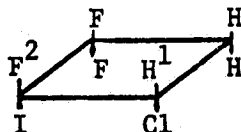
A proton-proton decoupled spectrum was identical to the spectrum of Figure A6. This indicates that all coupling was due to hydrogen-fluorine interaction and that no compound contained more than one hydrogen atom. The coupling constants and the relative areas were similar for peak set 4 of the  $^{19}\text{F}$  spectrum and peak set 8 of the proton spectrum, indicating that they can be attributed to the same compound. This compound was most likely the  $\text{C}_4\text{HCl}_6\text{F}$  molecule observed in the GC-MS analysis. The observed H-F coupling constant of 8.7-8.9 Hz suggests a vicinal H-F position.

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From the position of the doublet on the proton spectrum (5.14 ppm) it appears as though the proton of  $C_4HCl_6F$  is more shielded than the proton of  $CHCl_2-CClF_2$  (5.78 ppm). Therefore, the proton of  $C_4HCl_6F$  has less halogens in its vicinity than that of  $CHCl_2-CClF_2$ . Possible structures are shown below:



The  $H^1-F^2$  coupling constant of a compound similar to the above cyclic compound,



was reported to be 6.8 Hz (A3). This shows an approximate agreement with the value obtained in this study.

Several of the minor peaks in both spectra were not identified and were probably due to higher molecular weight compounds.

The detailed product distribution given in Table 4 was determined from the GC analysis for run 1, given in Table 3, and the proton n.m.r. analysis. The total of the isomers F-122 and F-122a was used as a basis between the two analyses to determine the mole percent of  $C_4HCl_6F$  and the other compounds.

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APPENDIX 4. ELECTRON SPECTROSCOPY FOR  
CHEMICAL ANALYSIS (E.S.C.A.)

E.S.C.A. was used to determine the degree of fluorination of the solid polymeric products. The products samples were analyzed on a Varian IEE Spectrometer for carbon and fluorine. The carbon and fluorine spectra for a typical polyacrylic acid run are shown in Figures A8 and A9, respectively. Multiple peaks on the carbon spectrum arise from different types of carbon atoms. The peaks resulting from the more highly fluorinated carbon atoms will appear at a higher binding energy. The area under the carbon and fluorine peaks is proportional to the number of carbon and fluorine atoms present in the sample; however, the proportionality constant differs between the two. Therefore, relative fluorine to carbon ratios can be determined by taking the ratios of the fluorine area to carbon area ratios of the individual samples. For example, the fluorine and carbon area ratio for run 3 is 3.2. This is 3.6 times greater than the fluorine to carbon area ratio of run 2, sample b.

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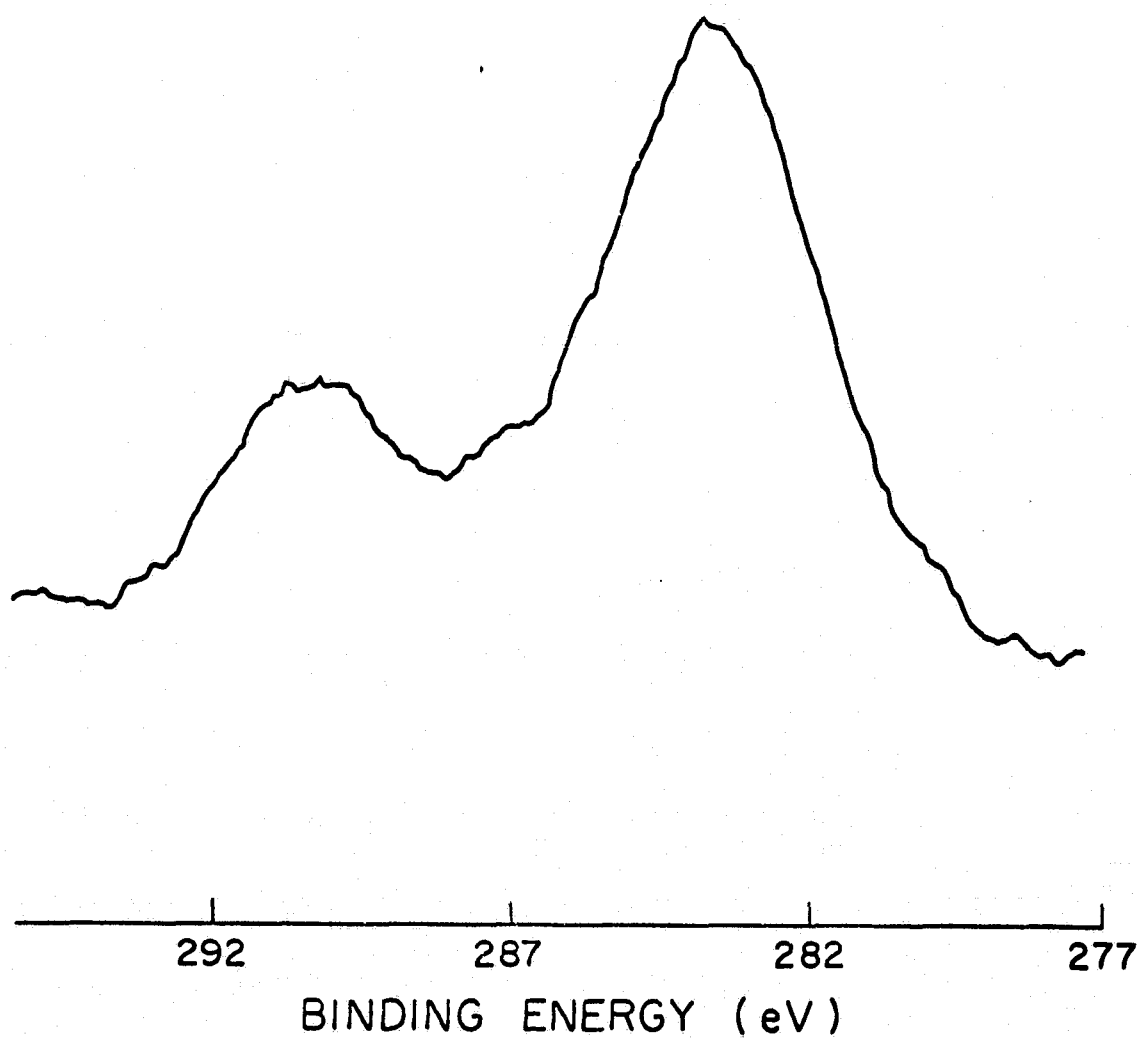


Fig. A8 Carbon Spectrum for a Typical E.S.C.A.  
Analysis of a PAA Run



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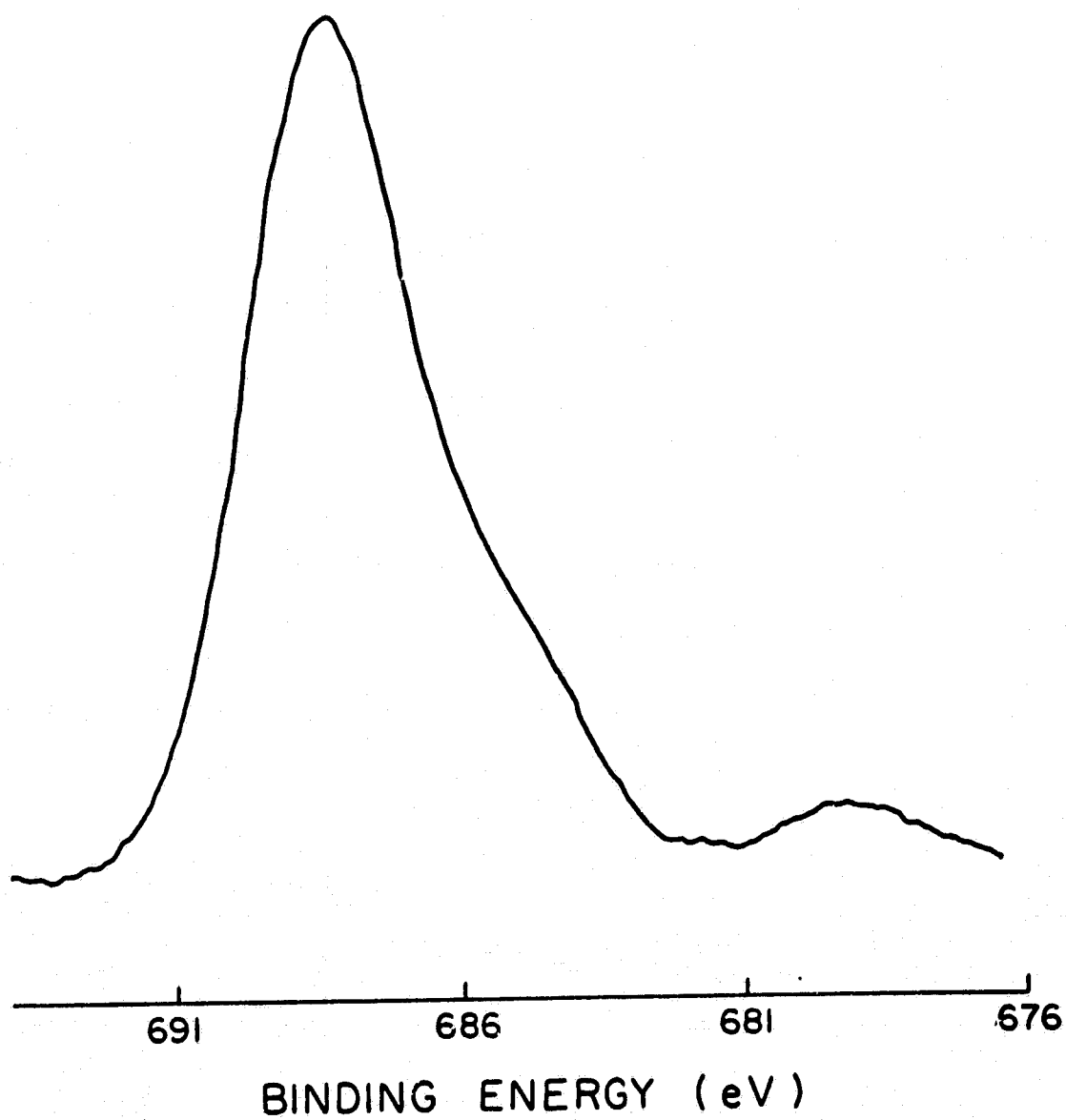


Fig. A9 Fluorine Spectrum for a Typical E.S.C.A.  
Analysis of a PAA Run

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APPENDIX 5. SAMPLE CURRENT EFFICIENCY CALCULATION  
FOR THE ELECTROCHEMICAL FLUORINATION  
OF TRICHLOROETHYLENE

As an example, the current efficiency calculation for run 4 of the electrochemical fluorination of trichloroethylene will be shown. Samples were taken at intermediate times and analyzed; the fluorinated product removed was accounted for in the calculations. Only the major two-carbon-chain products listed in Table 3 were considered. The product distribution for various reaction times is given in Table A4.

TABLE A4  
SUMMARY OF THE PRODUCT DISTRIBUTION AS A  
FUNCTION OF REACTION TIME FOR THE  
ELECTROCHEMICAL FLUORINATION  
OF TRICHLOROETHYLENE

Reaction Time, hrs	Product Composition, mole %			
	TCE	F-121	F-122 +F-122a	F-113
4.8	92.5	2.4	4.3	0.8
18.0	84.9	4.6	9.0	1.5
29.2	77.8	6.9	13.0	2.3
42.5	69.5	9.7	18.4	2.4
50.0	63.3	11.1	22.5	3.1

Physical properties of the major products are listed in Table A5. The current efficiency calculation is summarized in Table A6. The molar density is found by taking a weighted average of the molar density of each component. The molar density of the higher molecular weight compounds was not known and therefore, assumed to be the same as the mixture. For a reaction time of 4.8 hours:

$$\begin{aligned} \text{molar density} &= .925 \times .01116 + .024 \times .00873 + .043 \times .009198 \\ &+ .008 \times .008410 = 0.0110 \text{ mole/ml} \end{aligned}$$

$$\text{total moles in the reactor} = 0.0110 \frac{\text{mole}}{\text{ml}} \times 192 \text{ ml} = 2.11 \text{ moles}$$

The detailed product analysis showed that 20.8 mole percent of the product was  $\text{C}_4\text{HCl}_6\text{F}$  and other material. It was assumed for the current efficiency calculation that a similar amount of this material was present in all runs and that its mole percent increases linearly as a function of reaction time.

Hence,

$$\text{total moles of fluorine in two-carbon-chain products} =$$

$$2.11 \times \frac{100}{100 + 20.8} \times (1 \times .024 + 2 \times .043 + 3 \times .008)$$

$$= 0.234 \text{ moles}$$

$$\text{moles of fluorine removed in first sample} =$$

$$0.234 \times \frac{3.0 \text{ ml}}{192 \text{ ml}} = .0037 \text{ moles}$$

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TABLE A5  
PHYSICAL PROPERTIES OF THE MAJOR PRODUCTS FROM  
THE ELECTROCHEMICAL FLUORINATION  
OF TRICHLOROETHYLENE

Freon Code No.	Compound	Molecular Weight	Boiling Point, °C	Density, g/ml	Molar Density, mole/ml
F-1120	$\text{CHCl}=\text{CCl}_2$	131.4	87	1.446	0.011116
F-121	$\text{CHCl}_2-\text{CCl}_2\text{F}$	185.8	116.6	1.622	0.008730
F-122	$\text{CHCl}_2-\text{CClF}_2$	169.5	71.9	1.559	0.009198
F-122a	$\text{CHClF}-\text{CCl}_2\text{F}$	169.5	72.6	1.559	0.009198
F-113	$\text{CCl}_2\text{F}-\text{CClF}_2$	187.4	47.6	1.576	0.008410
F-C-321/F-321	$\text{C}_4\text{HCl}_6\text{F}$	280.8	-	-	-

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TABLE A6  
SUMMARY OF THE CURRENT EFFICIENCY CALCULATION

Reaction Time, hrs	Molar Density, mole/ml	Reactor Volume Before Sample, ml	Sample Size, ml	Moles of F Removed
4.8	0.0110	192	3.0	.004
18.0	0.0107	189	4.0	.010
29.2	0.0106	185	4.0	.014
42.5	0.0104	181	3.5	.017
50.0	0.0102	177.5	177.5	.983

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This calculation is done for each sample. A total of 1.03 moles of fluorine was produced in this run. Thus,

$$\text{theoretical current consumption} = 1.03 \text{ moles} \times 26.8 \frac{\text{A-hrs}}{\text{mole}}$$

$$= 27.6 \text{ A-hrs}$$

$$\text{current efficiency} = \frac{27.6 \text{ A-hrs}}{74.1 \text{ A-hrs}} \times 100 = 37.2\%$$

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LIST OF REFERENCES IN THE APPENDIX

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